PRACTICE PAPERS

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CHEMISTRY MONTHLY FOR
JEE (Main & Advanced) & PMTs

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Assertion & Reason

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Advances in Research in Medicine

We are back to Ayurveda. At least for postgraduate classes in Ayurveda, we have to use and compete with other systems, instrumental analysis to back up our conclusions.

Recently Dr Nita Forouhi and her group of scientists have found that people with risk of type 2 diabetes can reduce the risk by 28% by taking a lot of Yogurt (curd).

This work is from the Medical Research Council at the University of Cambridge. Apart from Yogurt, even low fat cheese also reduces the risk though it is not as effective as Yogurt. For most of the problems, Ayurveda advises only buttermilk and that too dilute and warm. The medicines given are not the same for the same problem for all. The characteristic of the person is divided into three and the medicine given according to a person.

To treat the patient and not the disease is also the slogan in the latest Cancer Research. With advances in medical research, Professor Fabrice Andre' of the Institute Gustave Roussy in Paris has conducted studies on 18 cancer centres in France. Analysis of biopsy samples including at least fifty percent cancer tumour cells were from 407 patients. Studies were to observe the alterations in the genome due to cancer. The idea of precision medicine is to take samples of someone's tumour, then find out the particular molecular faults that are driving it and then give them the right targeted treatment. Complications like cancer cells developing resistance to targeted drug treatments will have to be overcome. Even a few steps in the right direction is for a great purpose.

Our congratulations for their great work and we wish them all success.

Anil Ahlawat
Editor

CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions to these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM
Set 8

JEE MAIN/PMTS

1. A mixture of ethane and ethene occupies 40 L at 1.00 atm and 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, the mole fractions of ethane and ethene in mixture are respectively
   (a) 0.66, 0.34
   (b) 0.34, 0.66
   (c) 0.53, 0.47
   (d) 0.47, 0.53

2. Increasing order of bond strengths of the following species are
   C_2^+, O_2^{2+}, Be_2, C_2, O_2^{2-}, C_2^-
   (a) $C_2^+ < C_2 < C_2^- < O_2^{2-} < O_2^{2+} < Be_2$
   (b) $Be_2 < O_2^{2-} < C_2^- < C_2 < C_2^+ < O_2^{2+}$
   (c) $Be_2 < O_2^{2-} < C_2^+ < C_2 < C_2^- < O_2^{2+}$
   (d) $O_2^{2+} < C_2^- < C_2 < C_2^+ < O_2^{2-} < Be_2$

3. In the following conversion :

   $$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{\ 'X'\ } CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$$
   $$\xrightarrow{\ 'Y'\ } CH_3-CH=CH_2$$

   identify X and Y.

	X	Y
(a)	$K_2Cr_2O_7/H_2SO_4$	Dil · NaOH
(b)	$LiAlH_4$	Dil · HCl
(c)	Zn-Hg, HCl	Conc. H_2SO_4, Δ
(d)	$NaBH_4$, CH_3OH	Conc. H_2SO_4, Δ

4. When one mole of a monoatomic ideal gas at T K undergoes adiabatic change under a constant external pressure of 1 atm, volume changes from 1 L to 2 L. The final temperature in kelvin would be
   (a) $\dfrac{T}{(2)^{2/3}}$
   (b) $T + \dfrac{2}{3 \times 0.0821}$
   (c) T
   (d) $T - \dfrac{2}{3 \times 0.0821}$

5. If the emf of the cell
   $Zn\,|\,Zn^{2+}(0.1\ M)\,||\,Fe^{2+}(0.01\ M)\,|\,Fe$
   is 0.2905 V, then equilibrium constant for the cell reaction is
   (a) $10^{0.32/0.0591}$
   (b) $10^{0.32/0.0295}$
   (c) $10^{0.26/0.0295}$
   (d) $e^{0.32/0.0295}$

JEE ADVANCED

6. In the following reaction sequence :
   $$Na_2CO_3 \xrightarrow[H_2O]{SO_2} W \xrightarrow{Na_2CO_3} X \xrightarrow[\Delta]{Elemental\ S} Y \xrightarrow{I_2} Z$$
   W, X, Y and Z are respectively

(a) Na_2SO_3, $NaHSO_3$, $Na_2S_4O_6$, $Na_2S_2O_3$
(b) $Na_2S_2O_3$, $NaHSO_3$, Na_2SO_3, $Na_2S_4O_6$
(c) $NaHSO_3$, Na_2SO_3, $Na_2S_2O_3$, $Na_2S_4O_6$
(d) $NaHSO_4$, Na_2SO_4, $Na_2S_2O_3$, $Na_2S_4O_6$

COMPREHENSION

An organic compound (A) having molecular formula $C_5H_{10}O_2$ on reaction with Br_2 in the presence of phosphorus gives (X). Compound (X) has an asymmetric carbon atom and on dehydrobromination gives another compound (Y). (Y) does not show geometrical isomerism and on decarboxylation yields an alkene (Z). (Z) on ozonolysis gives two compounds out of which only one shows positive iodoform test.

7. Compound (A) is
   (a) $CH_3CH_2CH_2CH_2COOH$
   (b) $CH_3 — \overset{\overset{\displaystyle CH_3}{|}}{CH} — CH_2COOH$
   (c) $(CH_3)_3CCOOH$
   (d) $CH_3CH_2COOCH_2CH_3$

8. An alkene (Z) is
   (a) $CH_3CH = CHCH_3$
   (b) $(CH_3)_2C = CHCOOH$
   (c) $CH_3CH_2CH = CHCOOH$
   (d) $(CH_3)_2C = CH_2$

INTEGER VALUE

9. After classifying the following elements into isotopes, isobars and isotones,

   $^{40}_{20}Ca$, $^{39}_{19}K$, $^{16}_{8}O$, $^{77}_{32}Ge$, $^{78}_{34}Se$, $^{18}_{8}O$, $^{238}_{92}U$, $^{40}_{21}Sc$, $^{14}_{7}N$, $^{15}_{7}N$, $^{77}_{33}As$

   the value obtained by multiplying the number of pairs of isotones by number of pairs of isobars and then divided by number of pairs of isotopes is

10. A solution is obtained by mixing 0.1 mol of CH_3NH_2 (ionisation constant, $K_b = 5 \times 10^{-4}$) with 0.08 mol of HCl and volume is made up to 1 L. If concentration of H^+ ions of the resulting solution is $x \times 10^{-11}$ M, then the value of x is

Practice Paper 2014
JEE MAIN

Exam on 6th April

1. The electron gain enthalpies of B, C, N and O with negative sign are in the order
   (a) B < C < N < O
   (b) B < C < O > N
   (c) B < C > O > N
   (d) B > C < O < N

2.

   Product (C) would be

   (a)
   (b)
   (c)
   (d)
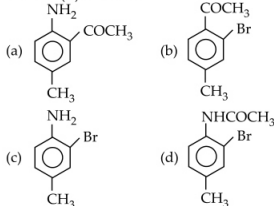
3. An electron has a velocity of 50 m s^{-1} accurate up to 99.99% .The uncertainty in locating its position is
   (a) 5.684×10^{-4} m
   (b) 1.369×10^{-6} m
   (c) 1.153×10^{-2} m
   (d) 4.523×10^{-5} m

4. In which of the following pairs of molecules/ions both the species are paramagnetic?
   (a) C_2, N_2^+
   (b) O_2^{2-}, F_2
   (c) NO, CN
   (d) N_2^{2-} NO^+

5. A compound with empirical formula CH_2O has a vapour density of 30. Its molecular formula is
   (a) $C_2H_2O_2$
   (b) $C_2H_4O_2$
   (c) $C_3H_6O_3$
   (d) $C_6H_{12}O_6$

6. If we add dilute aqueous solution of KI dropwise to $AgNO_3$ aqueous solution, the AgI colloid formed will have

   (a) negative charge
   (b) positive charge
   (c) neutral
   (d) nothing can be predicted.

7. Which of the following compounds is not correctly named?
   (a)
   1, 2-Epoxypropane
   (b) $NH_2CH_2CH_2CH_2NH_2$
   Propane-1, 3-diamine
   (c)
   3, 4-*bis*(*N*-Methylamino)biphenyl
   (d)
   N-Phenyldimethylamine
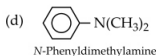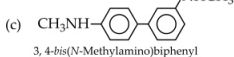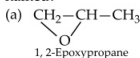
8. For H_3PO_3 and H_3PO_4, the correct choice is
   (a) H_3PO_3 is dibasic and reducing
   (b) H_3PO_4 is dibasic and non-reducing
   (c) H_3PO_4 is tribasic and reducing
   (d) H_3PO_3 is tribasic and non-reducing.

9. X, Y and Z are three elements forming a part of compound in oxidation states of +2, +5 and –2 respectively. What could be the compound?
   (a) $X_2(YZ)_2$
   (b) $X_2(YZ)_5$
   (c) $X_3(YZ_4)_2$
   (d) $X(YZ)_2$

10. Which one of the following reacts fastest with Na metal?
    (a) $C_6H_5-CH_2OH$
    (b)
    (c) F_3C-CH_2OH
    (d)
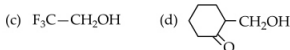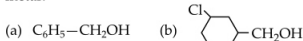
11. The vapour pressures of ethanol and methanol are 42.0 mm Hg and 88.5 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 46.0 g of ethanol with 16.0 g of methanol. The mole fraction of methanol in the vapour phase is
(a) 0.334   (b) 0.662
(c) 0.513   (d) 0.483

12. The mass of molecule A is twice the mass of molecule B. The rms speed of A is twice the rms speed of B. If two samples of A and B contain same number of molecules, the ratio of pressures of two samples A and B in separate containers of equal volume is
(a) 8   (b) 4   (c) 16   (d) 2

13. The acid containing $S-O-O-S$ bond is
(a) H_2SO_5 (b) $H_2S_2O_7$
(c) $H_2S_2O_6$ (d) $H_2S_2O_8$

14. An organic compound 'X' having molecular formula C_2H_3N on reduction gave another compound 'Y'. Upon treatment with nitrous acid, 'Y' gave ethyl alcohol. On warming with chloroform and alcoholic KOH, 'Y' formed an offensive smelling compound 'Z'. The compound 'Z' is
(a) $CH_3CH_2NH_2$ (b) $CH_3CH_2N{\equiv}C$
(c) $CH_3C \equiv N$ (d) CH_3CH_2OH

15. $E°$ values for Ti^{2+}/Ti, V^{2+}/V, Mn^{3+}/Mn^{2+}, V^{3+}/V^{2+} and Co^{3+}/Co^{2+} are -1.63 V, -1.18 V, $+1.57$ V, -0.26 V and $+1.97$ V respectively.
Identify the incorrect statement.
(a) Ti^{2+} and V^{2+} are strongest reducing agents and liberate hydrogen gas from dilute acids.
(b) Mn^{3+} and Co^{3+} are strongest oxidising agents in aqueous solution.
(c) Mn^{2+} is very stable due to the stable d^5 configuration.
(d) V^{2+} is less stable than V^{3+}.

16. When vapours of an alcohol are passed over hot reduced copper, it gives an alkene. The alcohol is
(a) primary   (b) secondary
(c) tertiary   (d) none of these.

17. Identify the wrong statement among the following.
(a) Acid rain is mostly because of oxides of nitrogen and sulphur.
(b) Chlorofluorocarbons are responsible for ozone layer depletion.
(c) Greenhouse effect is responsible for global warming.
(d) Ozone layer does not permit infrared radiations from the sun to reach the earth.

18. 3.92 g/L of a sample of ferrous ammonium sulphate reacts completely with 50 mL of $\dfrac{N}{10}$ $KMnO_4$ solution. The percentage purity of the sample is
(a) 50.0   (b) 78.4   (c) 80.0   (d) 39.2

19. The geometry of $[Ni(CO)_4]$ and $[Ni(PPh_3)_2Cl_2]$ are
(a) both square planar
(b) tetrahedral and square planar respectively
(c) both tetrahedral
(d) square planar and tetrahedral respectively.

20. If the solubility of lithium sodium hexafluoro aluminate, $Li_3Na_3(AlF_6)_2$ is 'S' mol/L, its solubility product is
(a) S^2 (b) $12\,S^2$
(c) $18\,S^3$ (d) $2916\,S^8$

**21.** Consider a reaction: $aP + bQ \rightarrow$ Products. When concentration of P is doubled keeping the concentration of Q fixed the rate increases 2 times.
When concentration of Q is doubled, keeping the concentration of P fixed, the rate increases 4 times. The overall order of the reaction is
(a) 1   (b) 2
(c) 3   (d) 2.5

22. The ionization energy of lithium is 520 kJ mol^{-1}. The amount of energy required to convert 210 mg of lithium atoms in gaseous state into Li^+ ions is
(a) -520 kJ   (b) 15.60 kJ
(c) 2.47 kJ   (d) -173.3 kJ

23. Which of the following is most stable?
(a) $Ph_3\overset{+}{C}$ (b) $Ph_2\overset{+}{C}H$
(c) $Ph\overset{+}{C}H_2$ (d) $(CH_3)_3\overset{+}{C}$

24. Consider the following structures :
(I) $CH_2=\overset{+}{C}H$ (II) $CH_3-\overset{+}{C}H_2$
(III) $CH_2=CH-\overset{+}{C}H_2$ (IV) $C_6H_5-\overset{+}{C}H-C_6H_5$
The correct sequence of these carbocations in the decreasing order of their stability is
(a) IV, III, II, I   (b) I, II, III, IV
(c) IV, II, III, I   (d) I, III, II, IV

25. In PO_4^{3-}, the formal charge on each oxygen atom and the $P-O$ bond order respectively are
(a) -0.75, 1   (b) -2, 1.0
(c) -0.75, 1.25   (d) -3, 1.25

26. Which of the following alkyl halides is hydrolysed by S_N2 mechanism?
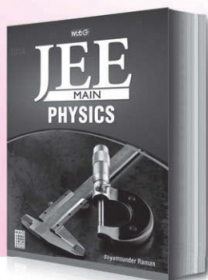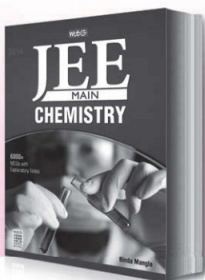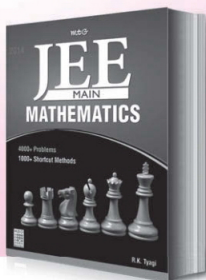
(a) $C_6H_5CH_2Br$ (b) CH_3Br
(c) $CH_2 = CHCH_2Br$ (d) $(CH_3)_3CBr$

27. The atomic numbers of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe) are 23, 24, 25 and 26 respectively. Which one of these may be expected to have the highest second ionisation enthalpy?
(a) V   (b) Cr   (c) Mn   (d) Fe

28. A molecule contains atoms P and Q so that P occurs at the corners of the cube while Q at the face centre. The formula of the molecule can be
(a) PQ_3 (b) P_3Q
(c) PQ_2 (d) P_2Q

29. If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then
(a) ΔH is –ve, ΔS is +ve
(b) ΔH and ΔS both are +ve
(c) ΔH and ΔS both are –ve
(d) ΔH is +ve, ΔS is –ve.

30. The correct order of decreasing acid strengths of different groups in the given amino acid is
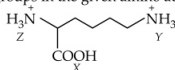
(a) $X > Z > Y$ (b) $Z > X > Y$
(c) $X > Y > Z$ (d) $Y > X > Z$

SOLUTIONS

1. **(b):** As we go from B → C → O, electron gain enthalpy becomes more negative due to decreasing size and increasing nuclear charge. The electron gain enthalpy of N is, however, positive because of the extra stability of the exactly half-filled $2p$-orbital. Thus, the overall sequence of electron gain enthalpy with negative sign is B < C < O > N.

2. **(c):**
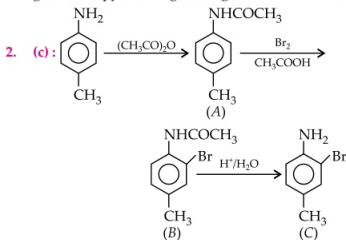
3. **(c):** By Heisenberg's uncertainty principle :

$$\Delta x \times m\Delta v \geq \frac{h}{4\pi}$$

Here, $m = 9.1 \times 10^{-31}$ kg,
$\Delta v = 50 \times (100 - 99.99)\%$
$= 50 \times 0.01 \% = \dfrac{50 \times 0.01}{100}$
$= 5 \times 10^{-3}$ m s^{-1}
$h = 6.6 \times 10^{-34}$ J s

$\therefore \quad \Delta x = \dfrac{h}{4\pi \times m \Delta v}$

$$= \frac{6.6 \times 10^{-34} \text{ Js}}{4 \times \frac{22}{7} \times 9.1 \times 10^{-31} \text{ kg} \times 5 \times 10^{-3} \text{ m s}^{-1}}$$

$$= \frac{6.6 \times 10^{-34} \text{ kg m}^2\text{s}^{-2} \text{ s} \times 7}{4 \times 22 \times 9.1 \times 10^{-31} \text{ kg} \times 5 \times 10^{-3} \text{ m s}^{-1}}$$

$[\because 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}]$

$= \dfrac{6.6 \times 7}{4 \times 22 \times 9.1 \times 5}$ m $= 1.153 \times 10^{-2}$ m

4. **(c):** Molecular orbital configuration of
$C_2 : \sigma 1s^2 \, \sigma^*1s^2 \, \sigma 2s^2 \, \sigma^*2s^2 \, \pi 2p_x^2 \, \pi 2p_y^2$ (diamagnetic)
$N_2^+ : \sigma 1s^2 \, \sigma^*1s^2 \, \sigma 2s^2 \, \sigma^*2s^2 \, \pi 2p_x^2 \, \pi 2p_y^2 \, \sigma 2p_z^1$ (paramagnetic)
$O_2^{2-} : \sigma 1s^2 \, \sigma^*1s^2 \, \sigma 2s^2 \, \sigma^*2s^2 \, \sigma 2p_z^2 \, \pi 2p_x^2 \, \pi 2p_y^2 \, \pi^*2p_x^2$ $\pi^*2p_y^2$ (diamagnetic)
$F_2 : \sigma 1s^2 \, \sigma^*1s^2 \, \sigma 2s^2 \, \sigma^*2s^2 \, \sigma 2p_z^2 \, \pi 2p_x^2 \, \pi 2p_y^2 \, \pi^*2p_x^2$ $\pi^*2p_y^2$ (diamagnetic)
$NO : \sigma 1s^2 \, \sigma^*1s^2 \, \sigma 2s^2 \, \sigma^*2s^2 \, \sigma 2p_z^2 \, \pi 2p_x^2 \, \pi 2p_y^2 \, \pi^*2p_x^1$ (paramagnetic)
$CN : \sigma 1s^2 \, \sigma^*1s^2 \, \sigma 2s^2 \, \sigma^*2s^2 \, \pi 2p_x^2 \, \pi 2p_y^2 \, \sigma 2p_z^1$ (paramagnetic)
$N_2^{2-} : \sigma 1s^2 \, \sigma^*1s^2 \, \sigma 2s^2 \, \sigma^*2s^2 \, \pi 2p_x^2 \, \pi 2p_y^2 \, \sigma 2p_z^2 \, \pi^*2p_x^1$ $\pi^*2p_y^1$ (paramagnetic)
$NO^+ : \sigma 1s^2 \, \sigma^*1s^2 \, \sigma 2s^2 \, \sigma^*2s^2 \, \sigma 2p_z^2 \, \pi 2p_x^2 \, \pi 2p_y^2$ (diamagnetic)

5. **(b):** Molecular weight = 2 × Vapour density
$= 2 \times 30 = 60$
$\therefore$ Molecular formula
$= \dfrac{\text{Molecular weight}}{\text{Empirical formula weight}} \times \text{E.F}$
$= \dfrac{60}{30} \times (CH_2O) = C_2H_4O_2$

6. **(b):** When KI solution is added to $AgNO_3$ solution, positively charged sol results due to adsorption of Ag^+ ions from dispersion medium.
AgI/Ag^+
Positively charged

7. (d) :
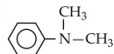
N, N-Dimethylbenzenamine
or N, N-Dimethylaniline

8. (a) :

H_3PO_3 H_3PO_4

Number of P — OH bonds determines the basicity of the acid and presence of P — H bond imparts reducing properties. Hence, H_3PO_3 is dibasic and reducing and H_3PO_4 is tribasic and non-reducing.

9. (c) : In compound $X_3(YZ_4)_2$, on substituting the oxidation states of each element the net oxidation state is found to be zero.

$3(+2) + 2(+5) + 8(-2) = 0$
$16 - 16 = 0$

10. (c) : More acidic alcohol will react faster with Na metal.

$F_3C - CH_2OH$ is strongest acid among the given alcohols because of $-I$ effect of three F atoms.

11. (c) : $p_{Total} = p_e° x_e + p_m° x_m$

where $n_e = \dfrac{46}{46} = 1$, $n_m = \dfrac{16}{32} = 0.5$

$x_e = \dfrac{1}{1.5} = \dfrac{2}{3}$, $x_m = \dfrac{0.5}{1.5} = \dfrac{1}{3}$

now $p_{Total} = 42 \times \dfrac{2}{3} + 88.5 \times \dfrac{1}{3} = 57.5$

$y_m = \dfrac{p_m}{p_{Total}}$ ($\because y_m =$ mole fraction of methanol in vapour phase)

where $p_m = p_m° \cdot x_m = 88.5 \times \dfrac{1}{3} = 29.5$

$y_m = \dfrac{29.5}{57.5} = 0.513$

12. (a) : Given, $M_A = 2M_B$ ...(i)
u_{rms} of $A = 2 \times u_{rms}$ of B ...(ii)
No. of molecules of $A =$ No. of molecules of B ...(iii)

For gas A, $P_A V_A = \dfrac{1}{3} M_A \left(u_{rms}^2\right)_A$

For gas B, $P_B V_B = \dfrac{1}{3} M_B \left(u_{rms}^2\right)_B$

$\therefore \dfrac{P_A V_A}{P_B V_B} = \dfrac{M_A}{M_B} \times \dfrac{u_A^2}{u_B^2}$ ...(iv)

$V_A = V_B$ ...(v)

$\therefore$ By equations (i), (ii), (iv) and (v),

$\dfrac{P_A}{P_B} = 2 \times (2)^2 = 8$

$P_A = 8P_B$

13. (d):
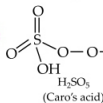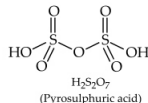
H_2SO_5 $H_2S_2O_7$
(Caro's acid)   (Pyrosulphuric acid)
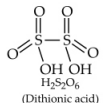
$H_2S_2O_6$ $H_2S_2O_8$
(Dithionic acid)   (Marshall's acid)

14. (b):
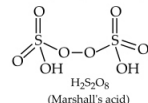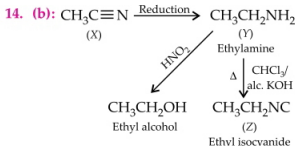
15. (d): Low value of $E°$ of V^{3+}/V^{2+} shows the stability of V^{2+} due to its half-filled t_{2g}^3 configuration.

16. (c) : Tertiary alcohols when passed over heated copper undergo dehydration to give alkenes.

17. (d): The thick layer of ozone called ozone blanket which is effective in absorbing harmful ultraviolet rays given out by the sun acts as a protective shield. It does not permit the ultraviolet rays from the sun to reach the earth.

18. (a) : $N_1 \times V_1 = N_2 \times V_2$
[FeSO$_4$.(NH$_4$)$_2$SO$_4$.6H$_2$O]   [KMnO$_4$]

$N_1 \times 1000 = \dfrac{1}{10} \times 50$ or $N_1 = \dfrac{1}{200}$
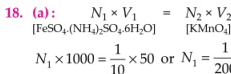
Eq. wt. of FeSO$_4$.(NH$_4$)$_2$SO$_4$.6H$_2$O = Mol. wt. = 392

$\therefore$ Strength of pure salt = $392 \times \dfrac{1}{200} = 1.96$ g L^{-1}

$\therefore$ % purity = $\dfrac{1.96}{3.92} \times 100 = 50\%$

19. (c) : Oxidation state of Ni in [Ni(CO)$_4$] = 0
Ni^0 (Z = 28): $3d^8 4s^2$
Since CO is strong field ligand, it forces electrons to pair up and thus sp^3 hybridisation takes place which results in tetrahedral geometry.
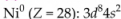
$[Ni(CO)_4] \rightarrow$
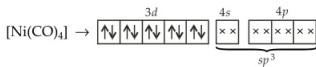
In $[Ni(PPh_3)_2Cl_2]$, oxidation state of Ni = +2.
This complex contains weak field ligand (Cl^-) as well as strong field ligand (PPh_3). Weak field ligand favours tetrahedral geometry and strong field ligand favours square planar geometry. Hence this compound is borderline between these two geometries. But due to steric effect of two larger PPh_3 ligands less crowded tetrahedral geometry is favoured.

$[Ni(PPh_3)_2Cl_2] \rightarrow$

20. (d): $Li_3Na_3(AlF_6)_2 \rightleftharpoons 3Li^+ + 3Na^+ + 2AlF_6^{3-}$
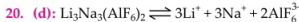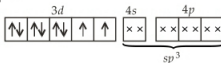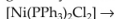
$\therefore \quad K_{sp} = [Li^+]^3[Na^+]^3[AlF_6^{3-}]^2$

$= (3S)^3 (3S)^3 (2S)^2 = 2916 \, S^8$

21. (c) : $r = k[P]^a [Q]^b$ \qquad …(i)

$2r = k[2P]^a [Q]^b$ \qquad …(ii)

$4r = k[P]^a [2Q]^b$ \qquad …(iii)

From equations (i) and (ii),

$\dfrac{2r}{r} = \dfrac{k[2P]^a[Q]^b}{k[P]^a[Q]^b}$

$2 = 2^a \Rightarrow (2)^1 = (2)^a \Rightarrow a = 1$

From equations (i) and (iii),

$\dfrac{4r}{r} = \dfrac{k[P]^a[2Q]^b}{k[P]^a[Q]^b}$

$4 = 2^b \Rightarrow (2)^2 = 2^b \Rightarrow b = 2$

Hence, a and b are 1, 2 respectively. The overall order of the reaction is $a + b = 1 + 2 = 3$.

22. (b): $Li_{(g)} \rightarrow Li_{(g)}^+$, I.E. = 520 kJ mol^{-1}
Mass of lithium = 210 mg = 210×10^{-3} g = 21×10^{-2} g
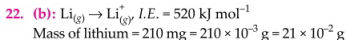
$\therefore$ Number of moles of lithium =

$\dfrac{21 \times 10^{-2}}{7} = 3 \times 10^{-2}$ mol

$\therefore$ Energy required to convert 3×10^{-2} mol atoms of lithium into Li^+ ions is

$= 520 \times 3 \times 10^{-2} = 15.60$ kJ

23. (a) : Greater the number of phenyl groups attached to the carbon atom bearing the positive charge, larger is the resonating structures, more stable is the carbocation.

24. (a)

25. (c) :
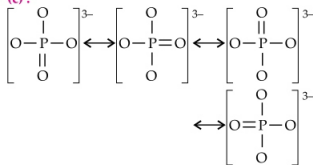
Three unit negative charge is being shared by four O atoms.

$\therefore$ Formal charge $= -3/4 = -0.75$

$\text{Bond order} = \dfrac{\text{Number of P—O bonds}}{\text{Number of resonating structures}}$

$= \dfrac{5}{4} = 1.25$

26. (b): In S_N2 reaction, since nucleophile attacks from the back side, hence the most favourable substrate will be primary alkyl halide due to least steric hindrance. More the number of alkyl groups more will be the steric hindrance for the approach of nucleophile to the carbon atom of C—X bond. Among the primary alkyl halides most favourable is methyl halide.

27. (b): The second ionisation potential value of Cr is sufficiently higher than those of neighbouring elements. This is because of the electronic configuration of Cr^+ which is $3d^5$ (half-filled), i.e., for the second ionisation, the electron is to be removed from very stable configuration.

28. (a): P atoms are at the corners of the cube,

$\therefore$ Number of P atoms per unit cell $= \dfrac{1}{8} \times 8 = 1$

Q atoms are at the face centre of the cube,

$\therefore$ Number of Q atoms per unit cell $= \dfrac{1}{2} \times 6 = 3$

$\Rightarrow$ The formula of the molecule is PQ_3

29. (b): For an endothermic reaction, $\Delta H = +ve$
Now, $\Delta G = \Delta H - T\Delta S$.
At freezing point of water i.e., at low temperature ΔG will be positive when ΔS is also positive.
At boiling point of water i.e., at high temperature ΔG will be $-ve$ when ΔS is also positive.

**30. (a):** In a given amino acid, —COOH group is stronger acid than —NH_3. Since —COOH has –I effect which decreases with distance, therefore, effect is more pronounced on Z than on Y. As a result Z is more acidic than Y. Therefore, overall order of decreasing acid strengths is $X > Z > Y$.

AIPMT Special

1. The equivalent conductivity of 0.05 N solution of a monobasic acid is 15.8 mho cm^2 eq^{-1}. If equivalent conductivity of the acid at infinite dilution is 350 mho cm^2 eq^{-1}, the dissociation constant of acid is
(a) 1.293×10^{-5}
(b) 1.642×10^{-4}
(c) 1.019×10^{-4}
(d) 1.392×10^{-5}

2. Identify the pair of species in which the central atom has the same type of hybridisation.
(a) BF_3 and NCl_3
(b) H_2S and $BeCl_2$
(c) NCl_3 and H_2S
(d) SF_4 and $BeCl_2$

3. The major product of the following reaction is
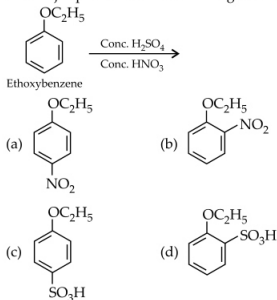
4. Al_2O_3 on heating with carbon in an atmosphere of Cl_2 at high temperature produces
(a) $Al + CO_2$
(b) $Al + CO_2 + NO$
(c) $Al_4C_3 + CO_2$
(d) $AlCl_3 + CO$

5. In the following reaction p, q, r and s are respectively
$$KMnO_4 + H_2SO_4 + CH_3CH_2OH \longrightarrow$$
$$pK_2SO_4 + qMnSO_4 + rCH_3CHO + sH_2O$$
(a) 2, 1, 3 and 7
(b) 1, 2, 5 and 8
(c) 5, 3, 4 and 2
(d) 7, 3, 1 and 6
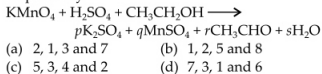
6. Which of the following statements is not the characteristic of zinc?
(a) It is a volatile metal.
(b) Its hydroxide dissolves in alkali forming sodium zincate.
(c) It is brittle at very high temperature.
(d) Zinc dust is used as a reducing agent.

7. The cubic unit cell of aluminium (molar mass 27.0 g mol^{-1}) has an edge length of 405 pm and density 2.70 g cm^{-3}. What type of unit cell is it?
(a) Face-centred
(b) Body-centred
(c) Simple cubic
(d) None of these.

8. CO_2 is not isostructural with
(a) $HgCl_2$
(b) $SnCl_2$
(c) C_2H_2
(d) $ZnCl_2$

9. The Lewis structure of N_2H_2 shows
(a) a nitrogen-nitrogen triple bond
(b) each hydrogen has one non-bonding electron pair
(c) each nitrogen has two non-bonding electron pairs
(d) each nitrogen has one non-bonding electron pair.

10. Product formed on reaction of sulphanilic acid with bromine water is
(a) p-bromoaniline
(b) 2, 4, 6-tribromoaniline
(c) o-bromoaniline
(d) 2, 6-dibromoaniline.

11. The correct order of increasing bond lengths of the following species is

C_2^-	C_2^{2-}	C_2
I	II	III

(a) I < III < II
(b) II < III < I
(c) II < I < III
(d) III < II < I

12. An endothermic reaction, $A \rightarrow B$ has an activation energy as x kJ mol^{-1}. If energy change of the

reaction is y kJ, the activation energy of the reverse reaction is
(a) $-x$ (b) $x - y$
(c) $x + y$ (d) $y - x$

13. The two electrons have the following sets of quantum numbers,
$P : 3, 2, -2, +1/2$ $Q : 3, 0, 0, +1/2$
Which of the following statements is true?
(a) P and Q have same energy.
(b) P has greater energy than Q.
(c) P has lesser energy than Q.
(d) P and Q represent same electron.

14. The first line in the Balmer series in the H-atom will have the frequency
(a) 4.57×10^{14} s^{-1} (b) 3.89×10^{15} s^{-1}
(c) 7.53×10^{15} s^{-1} (d) 8.15×10^{13} s^{-1}

15. The concentration at which degree of dissociation of a 0.2 M solution of CH_3COOH becomes double is (K_a of $CH_3COOH = 1.8 \times 10^{-5}$)
(a) 0.1 M (b) 0.009 M
(c) 0.4 M (d) 0.049 M

16. Which one of the following statements is not true?
(a) Ampicillin is a natural antibiotic.
(b) Aspirin is both analgesic and antipyretic.
(c) Sulphadiazine is a synthetic antibacterial drug.
(d) Some disinfectants can be used as antiseptics.

17. The activation energy of a reaction is 5 kcal/mol. The increase in the rate constant when its temperature is raised from 300 K to 310 K is approximately
(a) 15% (b) 50%
(c) 100% (d) 31%

18. NH_3 gas is liquefied more easily than N_2. Hence
(a) van der Waals' constants a and b of NH_3 is greater than that of N_2
(b) van der Waals' constants a and b of NH_3 is smaller than that of N_2
(c) $a(NH_3) > a(N_2)$ but $b(NH_3) < b(N_2)$
(d) $a(NH_3) < a(N_2)$ but $b(NH_3) > b(N_2)$.

19. Which of the following complexes will give maximum number of isomers?
(a) $[Co(NH_3)_4Cl_2]$ (b) $[Ni(en)(NH_3)_4]^{2+}$
(c) $[Ni(C_2O_4)(en)_2]^{2-}$ (d) $[Cr(SCN)_2(NH_3)_4]^+$

20. For the adsorption of a gas on a solid, the plot of $\log(x/m)$ versus $\log P$ is linear with slope equal to
(a) n (b) $1/n$
(c) k (d) $\log k$

21. Number of possible alkynes with the formula C_5H_8 is
(a) 2 (b) 3
(c) 4 (d) 5

22. The structure of *neo* pentyl group in an organic compound is
(a) $CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}$
$\quad\quad\quad\quad\quad\quad\quad\quad CH_3$
(b) $CH_3{-}CH_2{-}CH{-}CH_2{-}$
$\quad\quad\quad\quad CH_3$
(c) $CH_3{-}C{-}CH_2{-}$
$\quad\quad\quad CH_3$
(d) $CH_3{-}CH{-}CH_2{-}CH_2{-}$
$\quad\quad\quad CH_3$

23. Which of the following does not show tautomerism?
(a) $C_6H_5COCH_3$ (b) CH_3CHO
(c) CH_3COCH_3 (d) $C_6H_5COC(CH_3)_3$

24. The correct order of ionic radii of Y^{3+}, La^{3+}, Eu^{3+} and Lu^{3+} is
(a) $Y^{3+} < La^{3+} < Eu^{3+} < Lu^{3+}$
(b) $Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$
(c) $Lu^{3+} < Eu^{3+} < La^{3+} < Y^{3+}$
(d) $La^{3+} < Eu^{3+} < Lu^{3+} < Y^{3+}$

25. The intermetallic compound LiAg crystallizes in cubic lattice in which both lithium and silver have coordination number of eight. The crystal class is
(a) face-centred cube (b) simple cube
(c) body-centred cube (d) none of these.
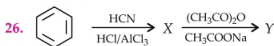
26.
Benzene

X and Y are respectively

(a)

(b)

(c)

(d)

27. Which of the following complexes has the least molar conductivity in the solution?
    (a) $CoCl_3 \cdot 3NH_3$ (b) $CoCl_3 \cdot 4NH_3$
    (c) $CoCl_3 \cdot 5NH_3$ (d) $CoCl_3 \cdot 6NH_3$

28. Bubble gum contains
    (a) thiokol rubber
    (b) styrene-butadiene rubber
    (c) isobutylene-isoprene rubber
    (d) acrylonitrile-butadiene rubber.

29. Silica is reacted with Na_2CO_3. Which gas is liberated?
    (a) CO (b) O_2
    (c) CO_2 (d) O_3

30. Aluminium oxide may be electrolysed at 1000° C to furnish aluminium metal (At. mass = 27 amu, 1 faraday = 96500 coulombs). The cathode reaction is
    $$Al^{3+} + 3e^- \longrightarrow Al$$
    To prepare 5.12 kg of aluminium metal by this method would require
    (a) 5.49×10^4 C of electricity
    (b) 5.49×10^1 C of electricity
    (c) 5.49×10^7 C of electricity
    (d) 1.83×10^7 C of electricity.
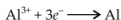
31. An acid solution has a pH = 6. It is diluted 100 times, the pH of the resultant solution would be
    (a) 5.95 (b) 6.95
    (c) 7 (d) 8

32. Which of the following alkenes is least reactive towards anionic polymerization?
    (a) $H_2C=CHCH_3$ (b) $H_2C=CF_2$
    (c) $H_2C=CHCN$ (d) $H_2C=CHC_6H_5$

33. Which of the following is most acidic in nature?
    (a) SiO_2 (b) N_2O_5
    (c) SO_3 (d) CO_2

34. The r.m.s. velocity of CO_2 at a temperature T (in K) is x cm s^{-1}. At what temperature (in K), the r.m.s. velocity of nitrous oxide would be $4x$ cm s^{-1}?
    (a) $16 T$ (b) $2 T$
    (c) $4 T$ (d) $32 T$
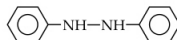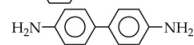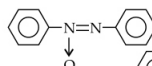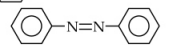
35. Osmotic pressure of blood is 7.65 atm at 310 K. The aqueous solution of glucose is isotonic with blood if its concentration is (wt./vol.)
    (a) 53.4 g/L (b) 35.4 g/L
    (c) 54.1 g/L (d) 25.33 g/L

36. $C_6H_5NO_2 \xrightarrow[NH_4Cl]{Zn\ dust} A \xrightarrow[Conc.\ HCl]{Cold} B$
    A and B respectively are
    (a)
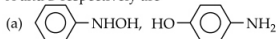
37. Which of the following is incorrect?
    (a) (b)
    (c) (d)

38. Which of the following has least covalent P—H bond?
    (a) PH_3 (b) P_2H_6
    (c) P_2H_5 (d) PH_6^+

39. The correct order of increasing boiling point is
    (a) 0.01 m $NaNO_3$ < 0.01 m $La(NO_3)_3$ < 0.01 m $MgBr_2$
    (b) 0.01 m $NaNO_3$ < 0.01 m $MgBr_2$ < 0.01 m $La(NO_3)_3$
    (c) 0.01 m $MgBr_2$ < 0.01 m $La(NO_3)_3$ < 0.01 m $NaNO_3$
    (d) 0.01 m $La(NO_3)_3$ < 0.01 m $MgBr_2$ < 0.01 m $NaNO_3$

40. Structure of the compound whose IUPAC name is 5-ethyl-6-methylcyclohex-2-en-1-one is
    (a) (b)
    (c) (d)
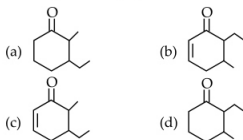
41. The wavelength of the radiation emitted producing a line in the Lyman series when an electron falls from fourth stationary state in hydrogen atom is
    ($R_H = 1.1 \times 10^7$ m^{-1})
    (a) 9.697×10^{-8} cm (b) 5.458×10^{-8} m
    (c) 5.458×10^{-8} cm (d) 9.697×10^{-8} m

42. What products are expected from the disproportionation reaction of hypochlorous acid?
    (a) $HClO_3$ and Cl_2O (b) $HClO_2$ and $HClO_4$
    (c) HCl and Cl_2O (d) HCl and $HClO_3$

43. $Zn + Cu^{2+}_{(aq)} \rightleftharpoons Cu + Zn^{2+}_{(aq)}$

Reaction quotient, $Q = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

Variation of E_{cell} with log Q is of the type given in graph with OA = 1.10 V, E_{cell} will be 1.1591 V when
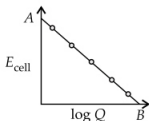
(a) $[Cu^{2+}]/[Zn^{2+}] = 0.1$ (b) $[Cu^{2+}]/[Zn^{2+}] = 0.01$
(c) $[Zn^{2+}]/[Cu^{2+}] = 0.01$ (d) $[Zn^{2+}]/[Cu^{2+}] = 0.1$

44. Which of the following have electrovalent, covalent and coordinate bonds?
(a) NH_4Cl (b) CO_2
(c) H_2O_2 (d) CH_4

45. How many π-electrons are there in the following structure?

(a) 2   (b) 4
(c) 6   (d) 8

SOLUTIONS

1. (c) : Degree of dissociation, $\alpha = \dfrac{\Lambda}{\Lambda^\circ}$

$\therefore \quad \alpha = \dfrac{15.8}{350} = 0.04514$

For monobasic acid, $HA \rightleftharpoons H^+ + A^-$

$K = \dfrac{C\alpha^2}{(1-\alpha)} = C\alpha^2$ $(\because \alpha << 1)$

$\therefore \quad K = 0.05 \times (0.04514)^2, \quad K = 1.019 \times 10^{-4}$

2. (c) : N atom in NCl_3 and S atom in H_2S are sp^3 hybridised.

3. (a) :

Ethoxybenzene → 2-Ethoxynitrobenzene (Minor) + 4-Ethoxynitrobenzene (Major)

4. (d) : $Al_2O_3 + 3C + 3Cl_2 \xrightarrow{1000°C} 2AlCl_3 + 3CO$

5. (b) : $2KMnO_4 + 3H_2SO_4 + 5CH_3CH_2OH \longrightarrow$
$\qquad K_2SO_4 + 2MnSO_4 + 5CH_3CHO + 8H_2O$

6. (c) : Zinc is slightly brittle at room temperature but more malleable at or above 100°C.

7. (a) : $\rho = \dfrac{Z \times M}{N_0 \times a^3}$

$Z = \dfrac{\rho \times N_0 \times a^3}{M}$

$Z = \dfrac{2.7 \times 6.023 \times 10^{23} \times (405 \times 10^{-10})^3}{27.0} = 4$

i.e., number of atoms per unit cell is 4. Hence, unit cell is face-centred type.

8. (b) : $SnCl_2$ is AB_2L type of structure in which two bond pairs and one lone pair of electrons are present. So, it forms bent (V-shape) structure.

9. (d) : $H-\overset{\cdot\cdot}{N}=\overset{\cdot\cdot}{N}-H$

10. (b) :

Sulphanilic acid $\xrightarrow{Br_2-water}$ 2, 4, 6-Tribromoaniline
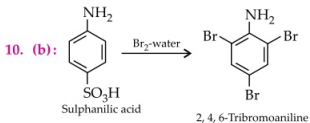
11. (c) : Total number of electrons in C_2 molecule is 12.

Its electronic configuration is
$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, (\pi 2p_x^2 = \pi 2p_y^2)$

Bond order $= \dfrac{1}{2}(8-4) = 2$

E.C. of $C_2^- = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, (\pi 2p_x^2 = \pi 2p_y^2)$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \pi 2p_z^1$

Bond order $= \dfrac{1}{2}(9-4) = 2.5$

E.C. of $C_2^{2-} = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, (\pi 2p_x^2 = \pi 2p_y^2)$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \pi 2p_z^2$

Bond order $= \dfrac{1}{2}(10-4) = 3$

Greater the bond order, shorter is the bond length. Therefore, order of bond lengths will be $C_2^{2-} < C_2^- < C_2$.

12. (b) :
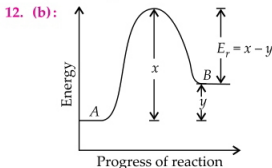
13. (b): P is $3d$ and Q is $3s$. Energy of $3s < 3d$.

14. (a) : Frequency of the first line in the Balmer series is

$$\upsilon = \frac{c}{\lambda} = c.\bar{\upsilon} = 3 \times 10^{10} \times 109677 \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] s^{-1}$$

$$= 3.29 \times 10^{15} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] s^{-1}$$

$$= 3.29 \times 10^{15} \left[\frac{1}{(2)^2} - \frac{1}{(3)^2}\right] = 3.29 \times 10^{15} \left[\frac{1}{4} - \frac{1}{9}\right]$$

$$= 3.29 \times 10^{15} \times \frac{5}{36} = 4.57 \times 10^{14} \, s^{-1}$$

15. (d): Since CH_3COOH is weak acid, so Ostwald's dilution law can be applied.

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.2}} = 9.5 \times 10^{-3}$$

When degree of dissociation becomes double i.e., 2α

$$C = \frac{K_a}{\alpha^2} = \frac{1.8 \times 10^{-5}}{(2 \times 9.5 \times 10^{-3})^2} = 0.049 \, M$$

16. (a) : Ampicillin is a modification of penicillin and thus is not a natural antibiotic. These semisynthetic penicillin (SSP) like ampicillin, cloxacillin, etc. are produced by chemically combining specific side chains (in place of benzyl side chain of penicillin group) or by incorporating specific precursors in the mold cultures. The aim of producing SSP's is to overcome penicillin's shortcomings such as poor oral efficacy, hyper sensitivity, susceptibility to penicillinase, narrow spectrum of activity, etc.

17. (d) : From Arrhenius equation

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log \frac{k_2}{k_1} = \frac{5000}{2.303 \times 2}\left(\frac{10}{310 \times 300}\right) = 0.1167$$

Antilog $(0.1167) = 1.308$

Hence $\frac{k_2}{k_1} = 1.308$

or $\frac{k_2}{k_1} - 1 = 1.308 - 1$; $\frac{k_2 - k_1}{k_1} = 0.308$

or $k_2 - k_1 = 0.308 \, k_1$

i.e. k_2 increases $= 30.8\% \approx 31\%$

18. (c) : More the value of a and lesser the value of b, the more easily the gas is liquefied.

19. (d) : $[Cr(SCN)_2(NH_3)_4]^+$ shows linkage, geometrical and optical isomerisms.

20. (b) : According to Freundlich adsorption isotherm,

$$\log\left(\frac{x}{m}\right) = \log k + \left(\frac{1}{n}\right) \log P$$

21. (b) : Possible isomers of C_5H_8 are
$$HC \equiv C - CH_2 - CH_2 - CH_3$$
$$HC \equiv C - CH - CH_3$$
$$\qquad\qquad\qquad | $$
$$\qquad\qquad\quad CH_3$$
$$CH_3 - C \equiv C - CH_2 - CH_3$$
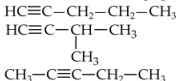
22. (c)

23. (d): $C_6H_5COC(CH_3)_3$ does not contain an α-hydrogen and hence does not show tautomerism.

24. (b): Ionic radii decrease from La^{3+} to Lu^{3+} due to lanthanoid contraction.
$Y(Z = 39)$ is a first member of $4d$-series so that Y^{3+} is smallest in size.
Thus order of ionic radii is $La^{3+} > Eu^{3+} > Lu^{3+} > Y^{3+}$.

25. (c) : A body-centred cubic unit cell consists of 8 atoms at the corners and one atom at the centre.

26. (c) :

Benzene $\xrightarrow[\text{HCl/AlCl}_3]{\text{HCN}}$ (X) Benzaldehyde (CHO) $\xrightarrow[\text{CH}_3\text{COONa}]{(\text{CH}_3\text{CO})_2\text{O}}$ (Y) Cinnamic acid (CH=CHCOOH)
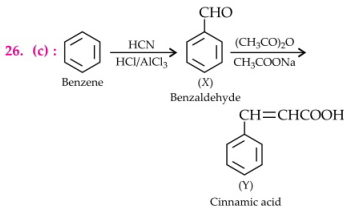
27. (a) : $CoCl_3 \cdot 3NH_3$ is $[Co(NH_3)_3Cl_3]$ which is non ionizable in solution.

28. (b): Bubble gum contains styrene-butadiene rubber.

29. (c) : $SiO_2 + Na_2CO_3 \xrightarrow{\Delta} Na_2SiO_3 + CO_2\uparrow$
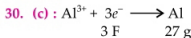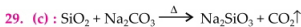
30. (c) : $Al^{3+} + 3e^- \longrightarrow Al$
$\qquad\qquad 3\,F \qquad\qquad 27\,g$
27 g of Al get deposited by $= 3 \times 96500$ C
5120 g of Al get deposited by $= \frac{3 \times 96500}{27} \times 5120$
$\qquad\qquad\qquad\qquad\qquad = 5.49 \times 10^7$ C

31. (b): pH = 6 or $H^+ = 10^{-6}$; when it is diluted 100 times.
i.e., $H^+ = 10^{-6} \times 10^{-2} = 10^{-8}$
But pH of an acid cannot exceed 7. Here we should also consider [H^+] that comes from water.

Now $[H^+] = [H^+]$ from HCl $+ [H^+]$ from H_2O
$= 10^{-8} + 10^{-7} = 10^{-8} + 10 \times 10^{-8} = 11 \times 10^{-8}$
pH $= -\log (11 \times 10^{-8}) = -[1.0413 - 8] = 6.9587$

32. (a) : Anionic polymerization involves the formation of carbanion intermediate. Alkene which yields least stable carbanion will be least reactive. Alkenes with electron withdrawing group are more reactive towards anionic polymerization due to stabilization of carbanion. Thus $CH_2\!=\!CHCH_3$ is least reactive having no electron withdrawing group.

33. (c) : $SiO_2 < CO_2 < N_2O_5 < SO_3$
In case of oxides of non-metals, the acid strength increases with increase in oxidation state. The oxidation states of various elements are Si = +4, C = +4, N = +5, S = +6 in the given oxides. Due to the small size of C-atom, CO_2 is more acidic than SiO_2.

34. (a) : $\dfrac{C_{rms(CO_2)}}{C_{rms(N_2O)}} = \sqrt{\dfrac{T_{CO_2} \times M_{N_2O}}{M_{CO_2} \times T_{N_2O}}}$

$\Rightarrow \dfrac{x}{4x} = \sqrt{\dfrac{T_{CO_2}}{44} \times \dfrac{44}{T_{N_2O}}} \Rightarrow T_{N_2O} = 16\ T_{CO_2}$

35. (c) : For isotonic solution, $p_{glucose} = p_{blood}$
$\therefore \quad pV = nRT$

$7.65 \times V = \dfrac{w}{180} \times 0.082 \times 310$

$\dfrac{w}{V} = 54.1$ g/L

36. (a) : $C_6H_5NO_2 \xrightarrow[NH_4Cl]{Zn\ dust} C_6H_5NHOH$
$\qquad\qquad\qquad\qquad\qquad (A)$
$\xrightarrow{HCl}$ HO—⟨ ⟩—NH$_2$
$\qquad\qquad (B)$

37. (d) : $CH_3\!-\!\overset{+}{N}\!\!\overset{O}{\underset{O^-}{\nwarrow}} \longleftrightarrow CH_3\!-\!\overset{+}{N}\!\!\overset{O^-}{\underset{O}{\nearrow}}$

$CH_3\!-\!\overset{+}{N}\!\!\overset{O}{\underset{O^-}{\nwarrow}} \rightleftharpoons CH_2\!=\!N\!\!\overset{OH}{\underset{O^-}{\nearrow}}$
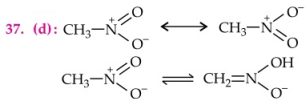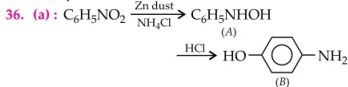
38. (d) : Due to the +ve charge on P, it attracts the electrons of the P—H bond towards itself. As a result, it has some ionic character. In other words, the P—H bond in PH_6^+ is least covalent.

39. (b) : ΔT_b being a colligative property depends upon the number of solute particles i.e. greater the number of ions larger will be the elevation in boiling point and thus greater will be the boiling point.
$La(NO_3)_3 \rightleftharpoons La^{3+} + 3NO_3^- \rightarrow 4$ ions

$MgBr_2 \rightleftharpoons Mg^{2+} + 2Br^- \rightarrow 3$ ions
$NaNO_3 \rightleftharpoons Na^+ + NO_3^- \rightarrow 2$ ions
$\therefore$ The correct order of increasing boiling point is
0.01 m $NaNO_3 < 0.01$ m $MgBr_2 < 0.01$ m $La(NO_3)_3$

40. (c) :

5-Ethyl-6-methylcyclohex-2-en-1-one

41. (d) : For Lyman series, $n_1 = 1$, but $n_2 = 4$ (given)

we know, $\bar{\upsilon} = R\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right] = 1.1 \times 10^7 \left[\dfrac{1}{1^2} - \dfrac{1}{4^2}\right]$

$\lambda = \dfrac{1}{\upsilon} = \dfrac{16}{15} \times \dfrac{1}{1.1 \times 10^7} = 9.697 \times 10^{-8}$ m

42. (d) : $3HClO_{(aq)} \longrightarrow HClO_{3(aq)} + 2HCl_{(aq)}$
It is a disproportionation reaction of hypochlorous acid where the oxidation number of Cl changes from +1 (in ClO^-) to +5 (in ClO_3^-) and –1 (in Cl^-).

43. (c) : $E_{cell} = E°_{cell} - \dfrac{0.0591}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

From the given plot, $OA = E°_{cell} = 1.10$ V

$1.1591 = 1.10 - \dfrac{0.0591}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

$\therefore \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]} = -2$

Taking antilog
$[Zn^{2+}]/[Cu^{2+}] = 0.01$

44. (a) : $\left[\begin{array}{c} H \\ | \\ H\!-\!N\!\rightarrow\!H \\ | \\ H \end{array}\right]^+ Cl^-$
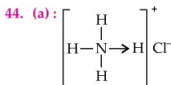
45. (c) :

Cyclopentadienyl anion
(planar, 6π electrons, aromatic)

COMPETITION CORNER

Organic Chemistry

Mukul C. Ray, Odisha

This time we have the chemistry of nitrogen containing organic compounds for you. This chapter is based on concepts, which are not new to you if you have studied the earlier chapters. However, from examination point of view, the chemistry of nitrogen compounds is extremely important. We have included all important points, which are there in the syllabus. One good reading and then you can move on to questions for practice.

Preparing Primary Amines

○ $R - X \xrightarrow{CN^-} R - CN \xrightarrow{\text{Reducing agent}} R - CH_2 - NH_2$
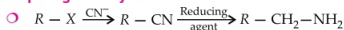
Reducing agents used are: H_2/Ni, $LiAlH_4$, Na/alcohol (Mendius reduction).

○ $R - NO_2 \xrightarrow{\text{Reducing agent}} R - NH_2$
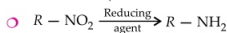
Reducing agents used are: $LiAlH_4$; Pt, Ni or Pd + H_2; $SnCl_2$ in HCl, Fe and H^+.

○ $R - X \xrightarrow{N_3^-} R - N_3 \xrightarrow{\text{Reducing agent}} R - NH_2$
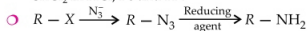
Reducing agents used are: $LiAlH_4$, Pt + H_2, $SnCl_2$ in HCl.

○ $\begin{matrix} R \\ R \end{matrix} C = N - OH \xrightarrow{\text{Reducing agent}} \begin{matrix} R \\ R \end{matrix} CH - NH_2$
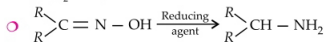
Reducing agents used are: Na + C_2H_5OH, $Ni/H_2 + NH_3$, $LiAlH_4$ followed by hydrolysis.

○ Reduction of nitrobenzene to aniline is the most important reaction of aromatic nitro compounds.

○—$NO_2 \xrightarrow{\text{Reducing agent}}$ ○—NH_2

Reducing agents used are: H_2 in the presence of Pd, Pt or Ni; Fe, Sn or Zn with mineral acid; $SnCl_2$ in HCl; N_2H_4 in the presence of Pd; sodium dithionite ($Na_2S_2O_4$); sodium and ammonium sulphides and polysulphides.

Again,

$$Ph - NO_2 \begin{cases} \xrightarrow[H_2O,\ NH_4Cl]{Zn} Ph - NHOH \\ \xrightarrow[H_2O]{Zn,\ NaOH} Ph - NH - NH - Ph \\ \xrightarrow[NaOH,\ H_2O]{As_2O_3} Ph - N \overset{O^-}{\underset{+}{=}} N - Ph \end{cases}$$

Reduction of nitrobenzene gives azobenzene (not aniline) with $LiAlH_4$.

$$Ph - NO_2 \xrightarrow[\text{2. } H_3O^+]{\text{1. } LiAlH_4} Ph - N = N - Ph$$
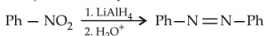
○ Carbonyl compounds can be converted to amines by first converting to imines and then reducing it by the use of several reducing agents.
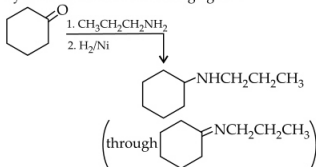
Instead of H_2/Ni, $NaBH_4$ in ethanol or $NaBH_3CN$ or $LiAlH_4$ in ether medium can be used.

○ Primary amines can also be prepared from Gabriel phthalimide synthesis.
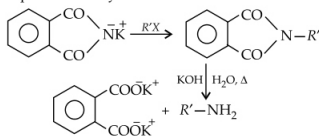
Note : $Ph - NH_2$, $(CH_3)_3CNH_2$ cannot be prepared by this method.

Reactions of Amines

$$R - X + NH_3 \longrightarrow R - \overset{+}{N}H_3X^-$$
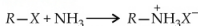
However, practically the reaction does not stop at

this stage. Ammonia present in the reaction flask deprotonates this, which then enters into further reaction.

$$R-\overset{+}{N}H_3X^- + NH_3 \longrightarrow R-NH_2 + \overset{+}{N}H_4X^-$$
$$\text{Free amine}$$

For example,

$$CH_3-CH_2-Br \xrightarrow[\substack{\text{2. NaOH (to neutralise} \\ \text{the amine salt)}}]{\substack{\text{1. 16-fold excess of } NH_3 \\ \text{in ethanol–}H_2O}}$$

$$CH_3-CH_2-NH_2 \ (34\%)$$
$$+$$
$$(CH_3-CH_2)_2NH \ (57\%)$$
$$+$$
$$(CH_3-CH_2)_3N \ (1\%)$$
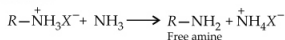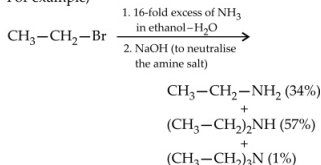
So, amine is not utilised as nucleophile except to produce 3° amine or quarternary ammonium salt.

While using a 2° amine to produce 3° amine, the product amine is sterically hindered and cannot attack further.

○ **Amines can initiate elimination :** In fact, 3° amines are often purposely used to carry out such elimination reactions.
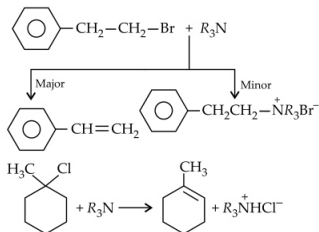
○ **Amines act as nucleophiles :** A little similar reaction is
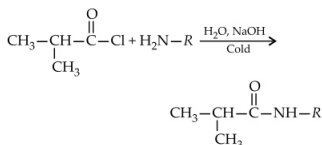
The success of this method is due to high nucleophilicity of amines, which competes successfully with hydroxide ion and water in attacking acyl halide. The less basic amide also does not permit it to undergo further acylation by acyl halides.
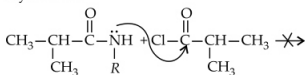
Note : Cyclic anhydride such as phthalic anhydride gives only a monamide.

○ **1° amines generate carbocations :** The reaction of amines with nitrous acid is a complex subject. Aliphatic primary amines react with nitrous acid to give a mixture of products.
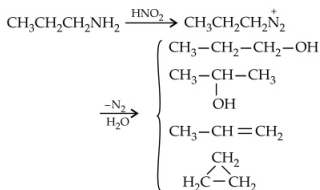
○ Cyclic amines can undergo ring expansion or ring contraction.
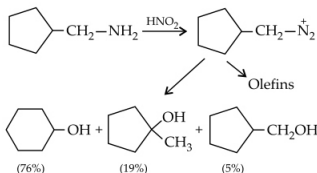
○ **2° amines do not give carbocation :** Secondary amines, both aliphatic and aromatic, react with nitrous acid to give yellow, neutral nitrosoamine.
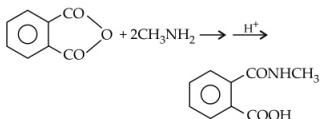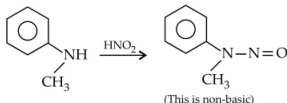
Very similar reaction is of acid chlorides of sulphonic acids with primary and secondary amines to give sulphonamides. This reaction forms the basis of classical Hinsberg's test.

Distinguishing 1°, 2° and 3° amines

○ To apply the Hinsberg's test, the amine is shaken with benzenesulphonyl chloride and aqueous alkali. If a homogeneous solution results, the amine is primary. If an insoluble material is present, the amine is either secondary (the insoluble material is secondary sulphonamide) or tertiary (the insoluble material is unreacted amine). To differentiate between the secondary and tertiary amines, the insoluble material is acidified. A tertiary amine will form a salt and dissolve while the secondary sulphonamide being neutral, remains insoluble.

$$R-NH_2 \xrightarrow{Ph-SO_2-Cl}$$
$$\text{1° Amine}$$

$$R-NH-\overset{\overset{\displaystyle O}{\|}}{\underset{\overset{\displaystyle \|}{O}}{S}}-Ph \xrightarrow{NaOH} R-\overset{-}{N}-\overset{\overset{\displaystyle O}{\|}}{\underset{\overset{\displaystyle \|}{O}}{S}}-Ph$$

Sulphonamide   (Water soluble)

$$\begin{array}{c} R \\ \diagdown \\ R \end{array} NH \xrightarrow[NaOH]{Ph-SO_2-Cl} \begin{array}{c} R \\ \diagdown \\ R \end{array} N-\overset{\overset{\displaystyle O}{\|}}{\underset{\overset{\displaystyle \|}{O}}{S}}-Ph$$
2° Amine

(Precipitate)

$$R_3N \xrightarrow[NaOH]{Ph-SO_2-Cl} PhSO_2\overset{+}{N}R_3Cl^-$$
3° Amine   (Hydrolysed very rapidly with water)
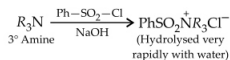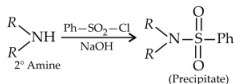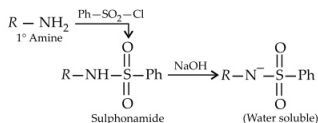
○ **3° amine reaction is unique :** In reaction of 3° amine with nitrous acid there may be several reactions considering hydrolysis also.

$$\begin{array}{c} H_3C \\ \diagdown \\ H_3C \end{array} N-CH_2-Ph + HNO_2 \longrightarrow \begin{array}{c} H_3C \\ \diagdown \\ H_3C \end{array} \overset{+}{N}-CH_2-Ph$$
$$\overset{|}{NO}$$

$$\xrightarrow{-HNO} \begin{array}{c} H_3C \\ \diagdown \\ H_3C \end{array} \overset{+}{N}=CH-Ph \xrightarrow{H_2O} \begin{array}{c} H_3C \\ \diagdown \\ H_3C \end{array} \overset{+}{NH_2} + Ph-CHO$$

Again,

$$\begin{array}{c} H_3C \\ \diagdown \\ H_3C \end{array} NH + HNO_2 \longrightarrow \begin{array}{c} H_3C \\ \diagdown \\ H_3C \end{array} N-N=O + H_2O$$
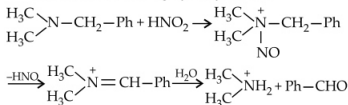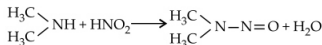
Also,

$$2HNO \longrightarrow H_2N_2O_2 \longrightarrow N_2O + H_2O$$
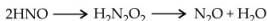
Amines react with carbonyl compounds

○ Primary and secondary amines add readily and reversibly to the carbonyl groups of most aldehydes and ketones to give carbinolamines, which undergo spontaneous dehydration, particularly in the presence of an acid, to give imines, frequently referred to as Schiff's bases.

$$R_2NH + O=CR_2' \rightleftharpoons R_2N-\overset{\overset{\displaystyle R'}{|}}{\underset{\overset{\displaystyle |}{OH}}{C}}-R'$$
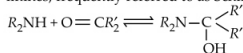
Undergoes spontaneous dehydration only if there is one α-hydrogen in the carbonyl part.

For example,

An enamine

Benzalaniline, a Schiff's base
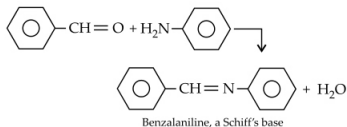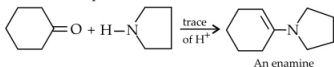
All types of amines are easily oxidised

○ The course of reaction is quite variable depends on the nature of the oxidising agent and the structure of amines. Only oxidation of tertiary amines is of major interest.

$$Ph-N\begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \end{array} \xrightarrow{H_2O_2} Ph-\overset{+}{\underset{\overset{\displaystyle |}{O}}{N}}\begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \end{array}$$
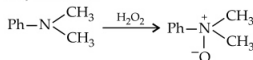
Secondary amine oxidation is followed by tautomerisation.
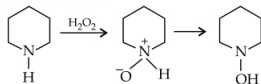
The oxidation of aliphatic primary amines usually produces a mixture of products: imines, enamines, nitriles and so on. It is rarely a reaction of preparative interest.

○ The oxidation of primary aromatic amines can also give very complex products. For example, mild chromic acid oxidation of aniline gives a polymer known as 'aniline black'. More vigorous oxidation of aniline gives benzoquinone.
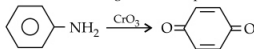
Peracids oxidise $-NH_2$ to $-NO_2$ group.

$$CH_3-\langle\bigcirc\rangle-NH_2 \xrightarrow{RCOOOH} CH_3-\langle\bigcirc\rangle-NO_2$$

Preparing alkene from amines

$$R-CH_2-CH_2-NH_2 \xrightarrow{H^+} R-CH=CH_2 + NH_3$$

No S_N1 or E1 possible because:

$$R_3C-\overset{+}{N}H_3 \rightleftharpoons R_3\overset{+}{C} + NH_3$$
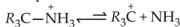
$C-N$ bond is much stronger than $C-O$ bond.
To prepare alkene we have a different procedure:
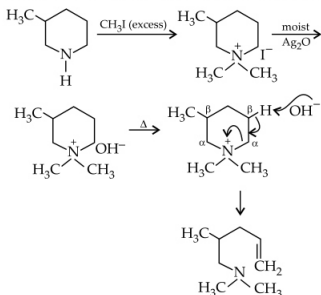
Proton abstraction takes place from the less crowded β-carbon giving less substituted alkene; a Hofmann product.
Crowding may alter the major course of reaction.

(Only 20%)
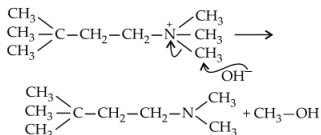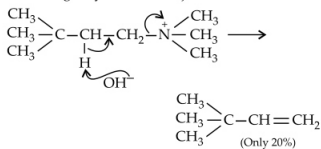
○ Certain reactions of imines, isocyanates, nitro compounds, enamines and cyanides are important.
The most characteristic reaction of imine is its hydrolysis reaction.

$$\overset{Ph}{\underset{Ph}{>}}C=NH \xrightarrow[HCl]{H_2O} \overset{Ph}{\underset{Ph}{>}}C=O + NH_4Cl$$
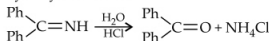
The simpler imines derived from ammonia are so unstable that they are known as **reactive intermediates.**

$$CH_3-CH=O \xrightarrow{NH_3} CH_3-CH=NH$$

Polymerises

(Acetaldimine trimer)

$$CH_2=O \xrightarrow{NH_3} CH_2=NH \longrightarrow$$

(Hexamethylenetetramine)
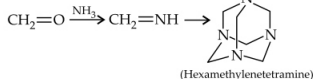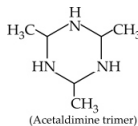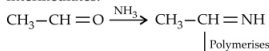
○ Secondary amine can be converted to tertiary amine by a mixture of HCOOH and formaldehyde. It is the Eschweiler–Clarke reaction.
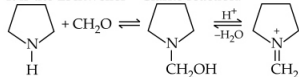
and then formic acid transfers a hydride.
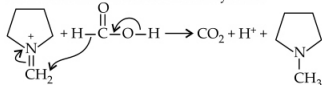
○ Isocyanates have the general formula $R-N=C=O$ which contains a carbon atom attached to 'N' as well as to 'O' by double bonds. It is attacked by variety of nucleophiles.

Isocyanate + Grignard's reagent $\xrightarrow{H_3O^+}$ Amide
Isocyanate + Amines $\longrightarrow$ Urea derivatives
Isocyanate + Alcohols $\longrightarrow$ Urethanes
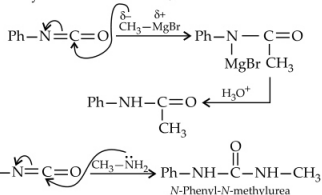
Isocyanates react readily with water.

$$R-N=C=O + H_2O \longrightarrow R-NH-COOH$$
$$\xrightarrow{-CO_2} R-NH_2$$
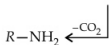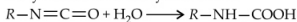
○ Enamines are excellent nucleophiles. A reactive alkyl or an acyl group can be easily introduced at the α-position to carbonyl group.
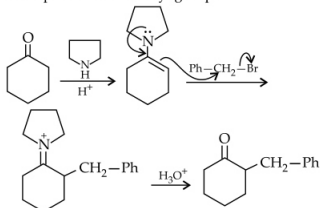
With simple alkyl halides such as CH_3CH_2Br, very little product of the above kind is obtained.

○ Cyanides are hydrolysed both in acidic and in basic medium. In basic medium, the hydrolysis is rather easier.
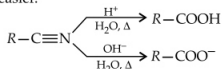
○ The hydrolysis of aromatic nitriles can be stopped at the amide stage. The aromatic cyanide is dissolved in conc. H_2SO_4 and then pouring acid solution into ice.

$$R-CN \xrightarrow[0°C]{H_2SO_4} R-\overset{+}{C}=NH \xrightarrow{H_2O} RCONH_2$$
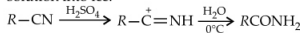
○ Ketone synthesis can be conveniently done using Grignard's reagent.
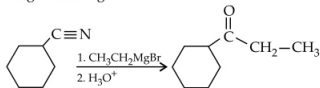
○ Nitriles having α-hydrogen can be alkylated. Indeed, monoalkylation of most nitriles is impractical.
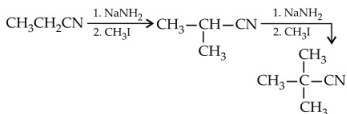
○ α,β-Unsaturated nitriles are usually good dienophiles in the Diels—Alder reaction.
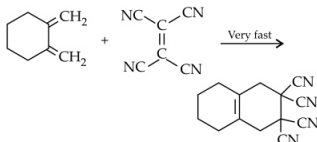
○ Careful neutralisation of a solution of nitronate anion affords a nitronic acid. Sometimes, known as an aci-nitro compound.

(aci-nitro compound)
Tautomer of nitro compound but more stable than enol form of a ketone.
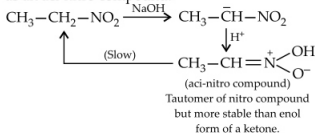
○ The reaction of nitronate ion with excess cold mineral acid does not give the nitronic acid but rather a carbonyl compound. This is the Nef reaction.

$$R-CH_2-NO_2 \xrightarrow{NaOH} \xrightarrow[H_2O]{H^+} R-CHO$$

$$R-\underset{R}{\underset{|}{CH}}-NO_2 \xrightarrow{NaOH} \xrightarrow[H_2O]{H^+} R-\underset{R}{\underset{|}{C}}=O$$
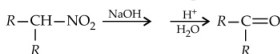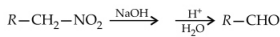
○ Nitro compounds with α-hydrogen act as nucleophiles.
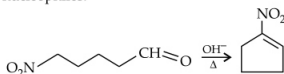
The reaction passes through a carbanion generation and then an intramolecular nucleophilic attack.
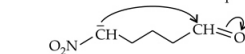
One more example to illustrate how nitro compound facilitates cabanion formation.
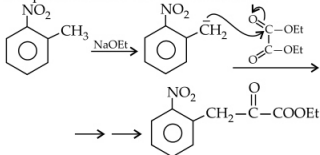
(Obtained as Na salt)

Y?U ASKED
WE ANSWERED

Q1. Which chemical is responsible for burning sensation that we get from chilli pepper sprays?

– *Prateek Khurana, Kurukshetra*

Ans. Capsaicin is the active ingredient of chilli pepper plants belonging to the genus *Capsicum*, having chemical name 8-methyl-*N*-vanillyl-6-nonenamide. It is colourless, odourless, crystalline to waxy and source of the hotness of pepper.
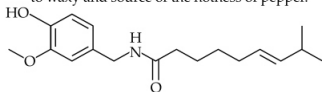
Capsaicin

It produces a burning sensation when it comes in contact with any tissue. Hence, now-a-days, it is used as pepper sprays, to ward off attacking muggers, dogs and bears.

Q2. What is 'Graphene'?

– *Smita Raisinghani, Meerut*

Ans. The 'miracle material' called graphene was discovered by Sir Andre Geim and Konstantin Novoselov. It consists of one-atom thick layer of carbon (graphite) arranged in two-dimensional, a honeycomb lattice. It is the thinnest as well as one of the strongest and hardest material in the world. Graphene possesses exceptional properties like, it is about 200 times stronger than steel and even stronger than diamond. It is highly flexible and conducts heat and electricity better than copper and silicon, thus also called 'silicon 2.0'. Currently, graphene is used in ink, airplane wings, DNA-sequencing devices, solar cells, anti-rust coatings, touch screens and even in living tissue applications.

Q3. Why does hot water freeze faster than cold water?

– *Vineeth Goel, Aligarh*

Ans. Hot water evaporates faster than cold water, thus reducing the amount of water left to be frozen. Formation of frost layer on cold water also insulates it from getting frozen faster. Hot water has less capacity to hold dissolved gases than cold water, which may affect its rate of freezing.

This can also be true on the basis of bonding. When the water warms up, the hydrogen bonds stretch and the water molecules move further apart. This allows the relaxation of covalent bonds, which causes water molecules to give up their energy. Hence, warm water cools faster than cold water.

Q4. Why do the teeth appear reddish and corroded for those people who chew betel leaves?

– *Sudarshan G.S., Mysore, Karnataka*

Ans. Teeth appear reddish and corroded for those people who chew betel leaves because of the presence of *katha* (catechu) which along with lime paste and areca nut is an important ingredient of 'paan'.

The areca nut reacts with lime paste to produce a narcotic called 'arecoline' which stimulates the parasympathetic nervous system for increased production of saliva.

Arecoline is an alkaloid found in the areca nut. It is an odourless oily liquid.
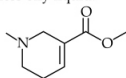
Methyl 1-methyl-1,2,5,6-tetrahydropyridine-3-carboxylate

Q5. What are Bose–Einstein and Fermionic condensates?

– *Nikita Arora, Delhi*

Ans. **Bose–Einstein Condensate (BEC)** is the 5th state of matter in which separate atoms or sub-atomic particles, cooled to near absolute zero (0 K, – 273.15°C, or – 459.67°F), coalesce into a single quantum mechanical entity. BECs are related to two remarkable low-temperature phenomena one is *superfluidity* (in which He[3] and He[4] forms a liquid with zero friction) and another is *superconductivity* (in which electrons move through a material with zero electrical resistance).

Fermionic condensate is the 6th state of matter. It is a superfluid phase formed by fermionic particles at low temperature. It is closely related to the Bose–Einstein condensate, a superfluid phase formed by bosonic atoms under similar conditions. Unlike the Bose–Einstein condensates, fermionic condensates are formed using fermions instead of bosons (sub-atomic particles smaller than an atom). *E.g.*, a chiral condensate.

Foundati◯n Series

JEE

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UNIT-9   Principles Related to Practical Chemistry

- **Practical Inorganic Chemistry :** Chemical principles involved in the qualitative salt analysis, chemistry involved in the preparation of the inorganic compounds.
- **Practical Organic Chemistry :** Detection of extra elements in organic compounds, detection of functional groups in organic compounds, chemistry involved in the preparation of the organic compounds.
- **Practical Physical Chemistry :** Chemistry involved in the titrimetric exercises, chemical principles involved in the physical chemistry experiments.

PRACTICAL INORGANIC CHEMISTRY

- Introduction
- Qualitative salt analysis

TIPS TO REMEMBER

❑ The qualitative salt analysis deals with the identification of acidic radicals (anions) and basic radicals (cations) in an inorganic salt or in a mixture of salts.

❑ In the salt, A_xB_y, A is positively charged ion and B is negatively charged ion.

$$\boxed{A_xB_y} \text{ Salt}$$

A^{y+} B^{x-}
Cation   Anion
(Basic radical)   (Acidic radical)
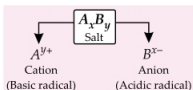
❑ It involves preliminary tests and wet tests.

Preliminary Tests

❑ It involves physical examination of salt like their characteristic colour and odour.

Test	Observation	Radicals
Colour	White	NH_4^+, Pb^{2+}, Al^{3+}, Zn^{2+}, Ba^{2+}, Ca^{2+}, Sr^{2+}, Mg^{2+}
	Blue	Cu^{2+}
	Green	Ni^{2+}, Cr^{3+}
	Light green	Fe^{2+}
	Brown	Fe^{3+}
	Pink	Co^{2+}
	Light pink (Flesh colour)	Mn^{2+}
Odour	Ammoniacal smell	NH_4^+
	Smell of vinegar	CH_3COO^-
	Smell of rotten eggs	S^{2-}

❑ Some tests like dry heating test, flame test, borax bead test, charcoal cavity test, cobalt nitrate test give preliminary idea of the radicals present in the salt.

Dry Heating Test

Observation	Radicals
Colourless gas evolved	CO_3^{2-}, SO_3^{2-}, S^{2-}, Cl^-
Brown gas evolved	Br^-, NO_3^-
Violet gas evolved	I^-
Crackling sound	$Pb(NO_3)_2$, $Ba(NO_3)_2$
Brown residue	Cu^{2+}

Flame Test

❑ Salt with 1 or 2 drops of conc. HCl is introduced in the non-luminous (oxidising part) flame of the Bunsen burner using platinum wire. Some basic radicals impart characteristic colour to the flame.

Colour of flame	Radicals
Golden yellow	Na^+
Lilac	K^+
Brick red	Ca^{2+}
Apple green	Ba^{2+}
Crimson red	Sr^{2+}
Greenish blue	Cu^{2+}

Borax Bead Test

❑ Borax is heated on a loop of Pt wire, colourless glassy bead of sodium metaborate and boric anhydride is formed.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta}$$
$$\underset{\text{Glassy bead}}{2NaBO_2 + B_2O_3}$$
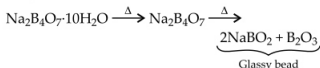
❑ Coloured salts are then heated on the glassy bead, coloured metaborate is formed in the oxidising flame.

$$CuSO_4 + B_2O_3 \longrightarrow \underset{\substack{\text{Copper metaborate} \\ \text{(Blue)}}}{Cu(BO_2)_2} + SO_3$$
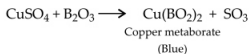
In reducing flame we have

$$2Cu(BO_2)_2 + C \longrightarrow 2CuBO_2 + B_2O_3 + CO$$
$$2Cu(BO_2)_2 + 2C \longrightarrow 2Cu + 2B_2O_3 + 2CO$$
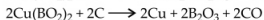
Hence different colours appear in different flames.

Metal	Colour in			
	Oxidising flame		Reducing flame	
	Hot	Cold	Hot	Cold
Copper	Green	Blue	Colourless	Brown red
Iron	Brown yellow	Pale yellow	Bottle green	Bottle green
Chromium	Yellow	Green	Green	Green
Cobalt	Blue	Blue	Blue	Blue
Manganese	Violet	Amethyst red	Colourless	Colourless
Nickel	Brown	Brown	Grey	Grey

Charcoal Cavity Test (Reduction test)

❑ Salt is heated with fusion mixture (Na_2CO_3 and K_2CO_3) in a charcoal cavity in reducing flame to form metallic oxides which are left as coloured residues. The colour of the residue being characteristic of the basic radical present.

Cobalt nitrate Test

❑ If the residue in charcoal cavity test is white, moisten it with a drop of cobalt nitrate and on heating in an oxidising flame, colour of the residue will change.

❑ Cobalt oxide, formed as a result of decomposition of cobalt nitrate, combines with metallic oxides to form coloured compounds, which are characteristic of basic radicals.

Key Points

❑ Some salts change colour on heating *e.g.*,

$$\underset{\text{Blue}}{CuSO_4 \cdot 5H_2O} \xrightarrow{\Delta} White$$

$$\underset{\text{Pink}}{CoCl_2} \xrightarrow{\Delta} Blue$$

$$\underset{\text{Green}}{Ni^{2+}} \xrightarrow{\Delta} Yellow$$
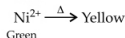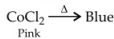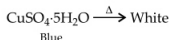
❑ Cobalt nitrate test should be performed with 2-3 drops of cobalt nitrate solution otherwise black cobalt oxide is formed which will mask the colour of the residue.

Wet Test

❑ **Identification of acidic radicals:** Most of the salts liberate gas on treating with dilute hydrochloric acid or dilute sulphuric acid and concentrated sulphuric acid.

❑ Some salts do not respond to any of these acids.
  ○ Depending on this behaviour, acidic radicals are divided into three groups:
    – *Group I :* This group consists of radicals which are detected by dilute H_2SO_4 or dilute HCl. These are (i) carbonate, (ii) sulphite, (iii) sulphide, (iv) nitrite and (v) acetate.
    – *Group II :* This group consists of radicals which are detected by concentrated H_2SO_4. These are (i) chloride, (ii) bromide, (iii) iodide, (iv) nitrate and (v) oxalate.
    – *Group III :* The radicals which do not give any characteristic gas with dilute and concentrated H_2SO_4. These are (i) sulphate, (ii) phosphate, (iii) borate and (iv) fluoride.

Group I acidic radicals : Salt + dilute HCl or dilute H_2SO_4

- Effervescence or evolution of gases indicates the presence of group I acidic radicals.

Observation	Gas	Radical	Reactions
Colourless, odourless gas turns limewater milky. Turbidity disappears on prolonged passage of gas.	CO_2	Carbonate (CO_3^{2-})	$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2\uparrow$ Salt $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$ Limewater, White ppt. (milky) $CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$ White ppt., Soluble
Colourless gas with smell of rotten eggs and turns lead acetate paper black. Gives violet coloured soluble complex with sodium nitroprusside solution.	H_2S	Sulphide (S^{2-})	$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S\uparrow$ Salt $(CH_3COO)_2Pb + H_2S \longrightarrow PbS\downarrow + 2CH_3COOH$ Black ppt. $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$ Sodium nitroprusside, Violet
Colourless gas with suffocating odour having smell of burning sulphur and turns acidified potassium dichromate solution green. White ppt. appears with barium chloride solution soluble in dilute hydrochloric acid.	SO_2	Sulphite (SO_3^{2-})	$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2\uparrow$ Salt $K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \longrightarrow$ $K_2SO_4 + Cr_2(SO_4)_3 + H_2O$ Green $Na_2SO_3 + BaCl_2 \longrightarrow BaSO_3\downarrow + 2NaCl$ Salt, White ppt. $BaSO_3 + 2HCl \longrightarrow BaCl_2 + H_2O + SO_2\uparrow$ White ppt., Soluble
Colourless gas followed by brown gas and turns ferrous sulphate solution brown.	NO_2	Nitrite (NO_2^-)	$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$ Salt, Nitrous acid $3HNO_2 \longrightarrow H_2O + 2NO + HNO_3$ $2NO + O_2 \longrightarrow 2NO_2\uparrow$ Brown $FeSO_4\cdot7H_2O + NO \longrightarrow [Fe(H_2O)_5NO]SO_4 + 2H_2O$ Brown
Colourless gas with smell of vinegar and turns neutral ferric chloride solution blood red. Gives smell of vinegar with oxalic acid.	CH_3COOH	Acetate (CH_3COO^-)	$2CH_3COONa + H_2SO_4 \longrightarrow 2CH_3COOH + Na_2SO_4$ Salt $3CH_3COONa + FeCl_3 \longrightarrow (CH_3COO)_3Fe + 3NaCl$ Salt, Blood red $2CH_3COONa + \begin{vmatrix} COOH \\ COOH \end{vmatrix} \longrightarrow \begin{vmatrix} COONa \\ COONa \end{vmatrix} + 2CH_3COOH$ Salt

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Key Points

❑ Sulphides of lead, cadmium, nickel, cobalt, antimony and tin are not decomposed by dilute H_2SO_4, therefore a pinch of zinc dust is added along with it. Conc. HCl should also be used.
$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$
$PbS + 2H \longrightarrow Pb + H_2S$

❑ Carbonates of bismuth and barium are not easily decomposed by dil. H_2SO_4. Dil. HCl should be used.

❑ Lead carbonate reacts with HCl or H_2SO_4 to give, in the initial stage, some effervescence but the reaction slows down due to the formation of a protective insoluble layer of $PbCl_2$ or $PbSO_4$ on the surface of remaining salt or mixture.

</div>

○ **Group II acidic radicals :** Salt + conc. H_2SO_4 or conc. HCl and heat (if necessary)
  – Effervescence or evolution of gases indicates the presence of group II acidic radicals.

Observation	Gas	Radical	Reactions
Colourless gas with pungent smell and gives white dense fumes with ammonium hydroxide. Gives white ppt. with silver nitrate solution soluble in ammonium hydroxide. Gives yellowish-green gas with suffocating odour on heating with manganese dioxide and concentrated sulphuric acid.	HCl	Chloride (Cl^-)	$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl\uparrow$ Salt $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$ White fumes $HCl + AgNO_3 \longrightarrow AgCl\downarrow + HNO_3$ White ppt. $AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl + 2H_2O$ White ppt. Soluble $2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2\uparrow$ Yellowish green
Brown gas which intensifies on addition of manganese dioxide. Gives pale yellow ppt. with silver nitrate solution partially soluble in ammonium hydroxide.	Br_2	Bromide (Br^-)	$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$ Salt $2HBr + H_2SO_4 \longrightarrow Br_2\uparrow + 2H_2O + SO_2$ Brown $2NaBr + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Br_2\uparrow$ Salt Brown $AgNO_3 + HBr \longrightarrow AgBr\downarrow + HNO_3$ Pale yellow ppt. $AgBr + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Br + 2H_2O$ Pale yellow ppt. Soluble
Deep violet gas which intensifies on adding manganese dioxide. Gives yellow ppt. with silver nitrate solution insoluble in ammonium hydroxide.	I_2	Iodide (I^-)	$2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$ Salt $2HI + H_2SO_4 \longrightarrow I_2\uparrow + SO_2 + 2H_2O$ Violet $2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2\uparrow$ Salt Violet $AgNO_3 + HI \longrightarrow AgI\downarrow + HNO_3$ Yellow ppt. $AgI + NH_4OH \longrightarrow$ Not soluble Yellow ppt.
Light brown gas having pungent smell, intensifies on adding copper turnings.	NO_2	Nitrate (NO_3^-)	$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$ Salt $4HNO_3 \longrightarrow 2H_2O + 4NO_2\uparrow + O_2$ Light brown fumes $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O$ Light brown fumes
Colourless, odourless gas which burns with blue flame and turns limewater milky.	CO + CO_2	Oxalate $(C_2O_4^{2-})$	$Na_2C_2O_4 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2C_2O_4$ Salt $H_2C_2O_4 + [H_2SO_4] \longrightarrow CO + CO_2 + H_2O + [H_2SO_4]$ Burns with Turns lime blue flame water milky

○ **Group III acidic radicals:** These radicals cannot be detected by either dil. H_2SO_4 or conc. H_2SO_4.
  For detection of these acidic radicals we need some specific tests.

Observation	Radical	Reactions
White ppt. is formed with barium chloride solution which is insoluble in concentrated nitric acid.	Sulphate (SO_4^{2-})	$Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow + 2NaCl$ Salt White ppt.

Yellow ppt. is formed with concentrated nitric acid and ammonium molybdate solution.	Phosphate (PO_4^{3-})	$Ca_3(PO_4)_2 + 6HNO_3 \longrightarrow 3Ca(NO_3)_2 + 2H_3PO_4$ Salt $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow$ $(NH_4)_3PO_4{\cdot}12MoO_3\downarrow + 21NH_4NO_3 + 12H_2O$ Canary yellow ppt.
Green edged flame on igniting the vapours evolved by heating the salt with ethyl alcohol and concentrated sulphuric acid.	Borate (BO_3^{3-})	$2Na_3BO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2H_3BO_3$ Salt $H_3BO_3 + 3C_2H_5OH \longrightarrow (C_2H_5)_3BO_3 + 3H_2O$ Ethyl borate
Waxy white deposit on the glass rod is formed when a small amount of salt with equal amount of sand is heated with concentrated sulphuric acid on placing a glass rod moistened with water.	Fluoride (F^-)	$2NaF + H_2SO_4 \longrightarrow Na_2SO_4 + H_2F_2$ Salt Hydrofluoric acid $SiO_2 + 2H_2F_2 \longrightarrow SiF_4 + 2H_2O$ Silica Silicon tetrafluoride $3SiF_4 + 4H_2O \longrightarrow H_4SiO_4 + 2H_2SiF_6$ Silicic acid (Gelatinous white)

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Key Points

☐ Test for fluoride should be performed in perfectly dry test tube, otherwise waxy white deposit will not be formed on the rod.

☐ $HgCl_2$ and NH_4Cl also produce a deposit under these conditions, but this deposit is crystalline in nature.

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Confirmatory Tests for Some Acidic Radicals

☐ **Chloride (Cl^-)**

○ *Chromyl chloride test :* On heating salt with concentrated sulphuric acid in the presence of potassium dichromate, deep red vapours of chromyl chloride are evolved.

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$
Salt
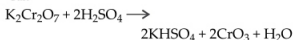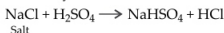
$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow$
$ 2KHSO_4 + 2CrO_3 + H_2O$
$CrO_3 + 2HCl \longrightarrow CrO_2Cl_2\uparrow + H_2O$
 Chromyl chloride
 (Red vapours)

These vapours on passing through sodium hydroxide solution give yellow solution of sodium chromate.

$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl$
 Yellow colour $ + 2H_2O$
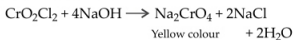
The yellow solution on neutralising with acetic acid and on adding lead acetate gives yellow precipitate of lead chromate.

$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow$
$ PbCrO_4\downarrow + 2CH_3COONa$
 Yellow ppt.

☐ **Bromide (Br^-)**

○ *Layer test :* On treating salt with dilute sulphuric acid, chloroform or carbon tetrachloride and chlorine water gives brown coloured layer.

Chlorine replaces bromine that dissolves in chloroform.

$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$
 Salt
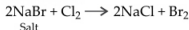
$Br_2 + Chloroform \longrightarrow$ Brown coloured layer

☐ **Iodide (I^-)**

○ *Layer test :* On treating salt with dilute sulphuric acid, chloroform or carbon tetrachloride and chlorine water, gives violet coloured layer.

Chlorine replaces iodine that dissolves in chloroform.

$2NaI + Cl_2 \longrightarrow 2NaCl + I_2$
 Salt
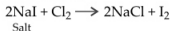
$I_2 + Chloroform \longrightarrow$ Violet coloured layer

○ *Starch paper test :* Violet vapours with starch paper give blue colour.

$I_2 + Starch \longrightarrow I_2$-starch complex
 Blue colour
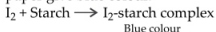
☐ **Nitrate (NO_3^-)**

○ *Brown ring test :* On treating aqueous solution of salt with freshly prepared solution of ferrous sulphate and concentrated sulphuric acid, gives a brown ring at the junction of two liquids.

$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$
 Salt

$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow$
$ 3Fe_2(SO_4)_3 + 4H_2O + 2NO$
$[Fe(H_2O)_6]SO_4{\cdot}H_2O + NO \longrightarrow$
Ferrous sulphate $ [Fe(H_2O)_5NO]SO_4 + 2H_2O$
 Brown ring
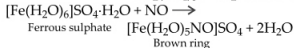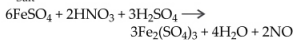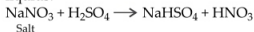
❑ **Oxalate ($C_2O_4^{2-}$)**
  ○ On acidifying sodium carbonate extract with acetic acid and on adding cadmium chloride solution gives white precipitate.
    Filter and dissolve the precipitate in dilute sulphuric acid and add few drops of potassium permanganate solution. The colour of potassium permanganate is discharged indicates the presence of oxalate.

$$Na_2C_2O_4 + CaCl_2 \longrightarrow CaC_2O_4\downarrow + 2NaCl$$
$\underset{\text{extract}}{\underset{\text{Sodium carbonate}}{}}$ $\qquad\qquad$ $\underset{\text{White ppt.}}{}$

$$CaC_2O_4 + H_2SO_4 \longrightarrow H_2C_2O_4 + CaSO_4$$
$$2KMnO_4 + 3H_2SO_4 \longrightarrow$$
$$\qquad\qquad K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\underset{\text{COOH}}{\overset{\text{COOH}}{|}} + [O] \longrightarrow 2CO_2 + H_2O$$
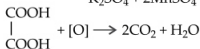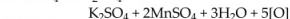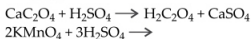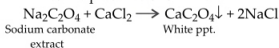
Key Points

❑ With conc. H_2SO_4, group I radicals behave in the same way as with dil. H_2SO_4.

❑ Before testing acetate with neutral ferric chloride solution, make sure that the solution is free from ions, carbonate, sulphite, phosphate and iodide as they combine with ferric ions.

❑ Chlorides of mercury, tin, silver, lead and antimony do not respond to chromyl chloride test. This test is performed by taking residue obtained after evaporation of sodium carbonate extract.

❑ Chromyl chloride test is performed in a dry test tube so that vapours of chromyl chloride do not get hydrolysed.
$$CrO_2Cl_2 + 2H_2O \longrightarrow H_2CrO_4 + 2HCl$$

❑ Brown ring test is not reliable in the presence of nitrite, bromide and iodide ions.

❑ While performing confirmatory test for oxalate, in presence of fluoride, a white precipitate of CaF_2 is also formed by the addition of $CaCl_2$ solution. But CaF_2 does not dissolve in dil. H_2SO_4 and does not discharge the colour of $KMnO_4$.

❑ While performing layer test for bromide and iodide ions, excess of chlorine water should be avoided.
  Under such conditions, the layer attains pale yellow colour due to the formation of bromine monochloride or becomes colourless due to the formation of hypobromous acid in case of bromide and iodic acid in case of iodide.
$$Br_2 + Cl_2 \longrightarrow \underset{\underset{\text{monochloride}}{\text{Bromine}}}{2BrCl}$$
$$Br_2 + 2H_2O + Cl_2 \longrightarrow \underset{\text{Hypobromous acid}}{2HBrO} + 2HCl$$
$$I_2 + 5Cl_2 + 6H_2O \longrightarrow \underset{\text{Iodic acid}}{2HIO_3} + 10HCl$$
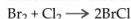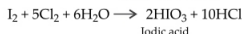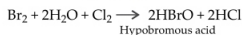
❑ **Identification of basic radicals :** Analysis of basic radicals involves three steps :
  ○ Preparation of the original solution of the salt or mixture.
  ○ Separation of basic radicals into different groups.
  ○ Analysis of the precipitates obtained in different groups and confirmation of the basic radicals.

Preparation of the Original Solution of the Salt or Mixture

❑ Original solution is prepared by using following solvents in the given order only.
  ○ Cold water
  ○ Hot water
  ○ Dilute HCl
  ○ Concentrated HCl

Separation of Basic Radicals into Different Groups

❑ For systematic analysis, the basic radicals are classified into different groups.

❑ Each group has specific reagent, which shows the presence of the basic radicals belonging to that particular group.

❑ Make sure that the radical is completely removed using excess of group reagent so that it does not create any difficulty in next group.

Group	Group reagent	Basic radical	Composition and colour of the precipitate	
I	Dilute HCl	Ag^+ Pb^{2+} Hg_2^{2+}	$AgCl$: white $PbCl_2$: white Hg_2Cl_2: white	Chlorides are insoluble in cold dilute HCl.

II	H_2S in presence of dilute HCl	Hg^{2+} Pb^{2+} Bi^{3+} Cu^{2+} Cd^{2+} As^{3+} Sb^{3+} Sn^{2+} Sn^{4+}	HgS : black PbS: black Bi_2S_3: black CuS: black CdS: yellow As_2S_3: yellow Sb_2S_3: orange SnS: brown SnS_2: yellow	Sulphides are insoluble in dilute HCl.
III	NH_4OH in presence of NH_4Cl	Fe^{3+} Cr^{3+} Al^{3+}	$Fe(OH)_3$: reddish brown $Cr(OH)_3$: green $Al(OH)_3$: white	Hydroxides are insoluble in NH_4OH.
IV	H_2S in presence of NH_4OH	Zn^{2+} Mn^{2+} Co^{2+} Ni^{2+}	ZnS: greenish white MnS: buff CoS: black NiS: black	Sulphides are insoluble in NH_4OH.
V	$(NH_4)_2CO_3$ in presence of NH_4OH	Ba^{2+} Sr^{2+} Ca^{2+}	$BaCO_3$: white $SrCO_3$: white $CaCO_3$: white	Carbonates are insoluble in NH_4OH.
VI	Na_2HPO_4 in presence of NH_4OH	Mg^{2+}	$Mg(NH_4)PO_4$: white	
Zero	NaOH	NH_4^+	Ammonia gas is evolved.	

Analysis of the Precipitates obtained in Different Groups and Confirmation of the Basic Radicals
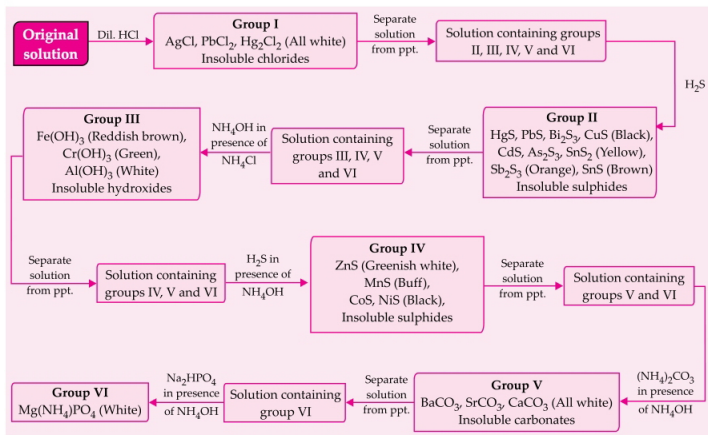
- Precipitation of basic radicals using group reagents in various groups depends on
  - *Common ion effect :* The ionization of a weak electrolyte or sparingly soluble salt is suppressed by the addition of another electrolyte containing a common-ion. This is known as common-ion effect.
  - *Solubility product :* For a salt, A_xB_y;
    $$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$
    If S is the solubility of A_xB_y, then
    $$K_{sp} = x^x y^y S^{x+y}$$

- K_{sp} is the ionic product when the solution is saturated.

Condition	Precipitation	Nature of solution
$K_{ip} > K_{sp}$	✓	Supersaturated
$K_{ip} < K_{sp}$	✗	Unsaturated
$K_{ip} = K_{sp}$	✗	Saturated (At equilibrium)

Group	Precipitate as	Explanation
I	Chlorides	K_{sp} values of chlorides of group I are low, hence their ionic products easily exceeds the solubility product and they get precipitated. Others have higher K_{sp} values hence not precipitated.
II	Sulphides	K_{sp} values of sulphides of group II are low, hence precipitated by low $[S^{2-}]$ ion. HCl (with common H^+ ion) decreases the ionization of H_2S which gives low $[S^{2-}]$. Hence, group II is precipitated. Others with higher K_{sp} values are not precipitated.
III	Hydroxides	K_{sp} values of hydroxides of group III are low. NH_4Cl (with common NH_4^+ ion) decreases the ionization of NH_4OH giving low $[OH^-]$. Hence, group III is precipitated.
IV	Sulphides	K_{sp} values of sulphides of group IV are high, hence precipitation takes place in higher $[S^{2-}]$. Basic medium increases the ionization of H_2S, thus increasing $[S^{2-}]$, hence precipitation of group IV occurs.
V	Carbonates	K_{sp} values of carbonates of group V are less than that of group VI (Mg^{2+}) hence group V is precipitated before Mg^{2+}.
VI	White ppt. $Mg(NH_4)PO_4$	—
Zero	—	Tested independently from original solution.

Preparation of Inorganic Compounds

- **Mohr's salt (Ferrous ammonium sulphate)**
  - It is a double salt containing ferrous sulphate and ammonium sulphate in equimolar amounts.
  - It is prepared by dissolving an equimolar mixture of hydrated ferrous sulphate and ammonium sulphate in water containing a little of sulphuric acid.
    $$FeSO_4 \cdot 7H_2O + (NH_4)_2SO_4 \longrightarrow$$
    $$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O + H_2O$$
- **Potash alum (*Phitkari*)**
  - It is a double salt containing potassium sulphate and aluminium sulphate in equimolar amounts.
  - It is prepared by dissolving an equimolar mixture of hydrated aluminium sulphate and potassium sulphate in water containing a little of sulphuric acid.
    $$K_2SO_4 + Al_2(SO_4)_3 \cdot 18H_2O + 6H_2O \xrightarrow{\Delta}$$
    $$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$
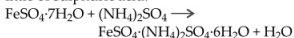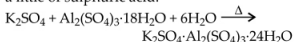
PRACTICAL ORGANIC CHEMISTRY

- Introduction
- Qualitative analysis

TIPS TO REMEMBER

Qualitative Analysis

- In addition to carbon and hydrogen, organic compounds may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.
- The qualitative analysis of organic compounds involves the detection of all these major elements present in it with the help of suitable chemical tests.

Detection of Extra Elements (N, S, halogens) in Organic Compounds

- The elements other than C, H and O are called extra elements.
- The elements are usually tested in the form of

ions. Since organic compounds are covalent in nature, they do not ionize. Therefore, to convert elements present in organic compounds into ions, the organic compound is fused with sodium metal which is plunged in distilled water, boiled and filtered.

○ The filtrate is called Lassaigne's extract or sodium extract.

Element	Detection	Confirmatory test	Reactions
Nitrogen	Lassaigne's extract (L.E.) $$Na + C + N \xrightarrow{\Delta} \underset{(L.E.)}{NaCN}$$	L.E. + $FeSO_4$ + NaOH, boil and cool + $FeCl_3$ + conc. HCl Gives blue or green colour.	$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$ $$Fe(OH)_2 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$$ $$Na_4[Fe(CN)_6] + FeCl_3 \xrightarrow{HCl} \underset{\text{Prussian blue}}{NaFe[Fe(CN)_6]} + 3NaCl$$ or $$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$
Sulphur	$$2Na + S \xrightarrow{\Delta} \underset{(L.E.)}{Na_2S}$$	(i) L.E. + sodium nitroprusside A deep violet colour. (ii) L.E. + CH_3COOH + $(CH_3COO)_2Pb$ Gives a black ppt.	(i) $$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow \underset{\text{Deep violet}}{Na_4[Fe(CN)_5NOS]}$$ $\underset{\text{Sodium nitroprusside}}{}$ (ii) $$Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH} \underset{\text{Black ppt.}}{PbS\downarrow} + 2CH_3COONa$$
Halogens	$$Na + Cl \xrightarrow{\Delta} \underset{(L.E.)}{NaCl}$$	L.E. + HNO_3 + $AgNO_3$ (i) White ppt. soluble in aq. NH_3 (or NH_4OH) confirms Cl. (ii) Yellow ppt. partially soluble in aq. NH_3 (or NH_4OH) confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 (or NH_4OH) confirms I.	$$NaX + AgNO_3 \xrightarrow{HNO_3} \underset{\text{White ppt.}}{AgX\downarrow}$$ $$\underset{\text{White ppt.}}{AgCl} + 2NH_{3(aq.)} \longrightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]Cl}$$
Nitrogen and sulphur together	$$Na + C + N + S \xrightarrow{\Delta} \underset{\substack{\text{Sodium} \\ \text{thiocyanate}}}{NaSCN}$$	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.	$$NaSCN + FeCl_3 \longrightarrow \underset{\text{Blood red colour}}{[Fe(SCN)]Cl_2} + NaCl$$

Key Points
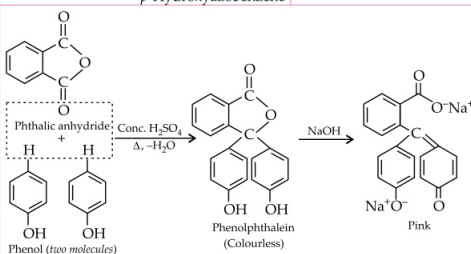
❑ When sodium fusion is carried out with excess of sodium, thiocyanate decomposes to cyanide and sulphide ions which give their usual tests. Thus, we do not get blood red colour with ferric chloride even though N and S both are present.

$$Na + C + N + S \longrightarrow \underset{\text{Sodium thiocyanate}}{NaCNS}$$

$$NaCNS + 2Na \longrightarrow NaCN + Na_2S$$
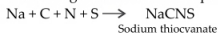
❑ Lassaigne's test fails in case of compounds which contain nitrogen but no carbon $e.g.$, hydrazine (NH_2NH_2) and hydroxylamine (NH_2OH).

Functional Group

❑ An atom or group of atoms that largely determines the properties of an organic compounds.

❑ **Detection of functional groups :** Hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl, amino and nitro groups in organic compounds.

Test	Reaction	Confirmation
(A) Detection of unsaturation		
(i) Baeyer's or KMnO$_4$ test	$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$ $\underset{}{>}C=C< + H_2O + [O] \longrightarrow >\underset{OH\ OH}{C-C}<$	Disappearance of pink colour of KMnO$_4$.
(ii) Br$_2$ - CCl$_4$ test	$\underset{\underset{brown}{Red}}{>}C=C< + Br_2 \xrightarrow{CCl_4} >\underset{Br}{\overset{Br}{C-C}}<$	Disappearance of brown colour.
(B) Detection of alcoholic group		
(i) Ester test	$RCOOH + R'-OH \xrightarrow[-H_2O]{conc.\ H_2SO_4} \underset{Ester}{RCOOR'}$	Fruity smell of ester indicates – OH group.
(ii) Ceric ammonium nitrate test	$2ROH + (NH_4)_2[Ce(NO_3)_6] \longrightarrow$ $\underset{Pink\ or\ red}{[(ROH)_2Ce(NO_3)_4] + 2NH_4NO_3}$	Appearance of pink or red colour.
(iii) Xanthate test	$ROH + KOH_{(s)} \xrightarrow{\Delta} \underset{Pot.\ alkoxide}{RO^-K^+ + H_2O}$ $RO^-K^+ + C\overset{S}{\underset{S}{=}} \longrightarrow R-O-C\overset{S^-K^+}{\underset{S}{=}}$ $\underset{\underset{(Yellow\ ppt.)}{Pot.\ alkyl\ xanthate}}{}$	Formation of yellow ppt.
(C) Detection of phenolic group		
(i) FeCl$_3$ test	$FeCl_3 + 6C_6H_5OH \longrightarrow$ $\underset{Violet}{[Fe(OC_6H_5)_6]^{3-} + 3H^+ + 3HCl}$	Appearance of violet colouration.
(ii) Azo dye test	$C_6H_5NH_2 + NaNO_2 + HCl \longrightarrow C_6H_5N_2^+Cl^-$ $C_6H_5N_2^+Cl^- + C_6H_5OH \xrightarrow[0-5°C]{pH\ 9-10}$ p-Hydroxyazobenzene	Formation of orange or red dye.
(iii) Phthalein test or fluorescein test		
	Appearance of green, blue, pink, purple or red fluorescent solution.	

(iv)	Br$_2$-H$_2$O test	 White ppt.	Appearance of white ppt.
(v)	Liebermann's nitroso test	$C_6H_5OH \xrightarrow[\text{H}_2\text{SO}_4]{\text{NaNO}_2} HO-C_6H_4-N=O$ p-Nitrosophenol $\xrightleftharpoons{\text{Tautomerises}}$ Quinone monoxime (Green) $\xrightarrow[\text{H}_2\text{SO}_4]{\text{Phenol}}$ Indophenol (Red) $\downarrow$ NaOH Indophenol sod. salt (Blue)	
		Appearance of deep blue or green colour which turns red on dilution and again blue on adding sodium hydroxide solution.	

(D) Detection of carbonyl group

Aldehydic/Ketonic group

(i)	Brady's reagent (2, 4-DNP) test	$\rightrightarrows C=O + H_2NNH-$ 2,4-Dinitrophenylhydrazine $\downarrow$ $\rightrightarrows C=NNH-$ Yellow, orange or red ppt.	Appearance of yellow, orange or red ppt.
(ii)	Sod. bisulphite test	$\rightrightarrows C=O + NaHSO_3 \longrightarrow$ White ppt.	Appearance of white ppt.

Aldehydic group

(i)	Tollens' test	$RCHO + 2[Ag(NH_3)_2]OH \longrightarrow$ $RCOONH_4 + 3NH_3 + H_2O + 2Ag_{(s)}$ Silver mirror	Formation of silver mirror along the sides of the test tube.
(ii)	Fehling's test	$RCHO + 2Cu^{2+} + 3OH^- \longrightarrow$ $2Cu^+\downarrow + RCOO^- + 2H_2O$ Red ppt.	A red ppt. is formed (only by aliphatic aldehydes).
(iii)	Schiff's test	$RCHO + p$-rosaniline hydrochloride (Colourless)	Appearance of pink colour.
(iv)	Benedict's test	$RCHO + 2Cu(OH)_2 + NaOH \longrightarrow$ $RCOONa + Cu_2O\downarrow + 3H_2O$ Red ppt.	Appearance of red ppt.

	Ketonic group		
(i)	Iodoform test	$R-CO-CH_3 + 3I_2 + 4NaOH \longrightarrow$ $3NaI + CHI_3\downarrow + RCOONa + 3H_2O$ Yellow ppt.	Formation of yellow ppt. of CHI_3 (for methyl ketones only).
(ii)	Sodium nitroprusside test	$RCOR$ + sodium nitroprusside solution + NaOH	Appearance of wine-red colour.

(E) Detection of carboxylic group

(i)	Litmus test	Blue litmus paper turns red.	–COOH group may be present.
(ii)	$NaHCO_3$ test	$RCOOH + NaHCO_3 \longrightarrow$ $RCOONa + H_2O + CO_2\uparrow$	Brisk effervescence of CO_2 indicates –COOH group.
(iii)	Ester test	$RCOOH + C_2H_5OH \xrightarrow[\Delta]{Conc.H_2SO_4}$ $RCOOC_2H_5 + H_2O$	Fruity smell of esters formed.
(iv)	$FeCl_3$ test	$3RCOOH + 3NH_4OH + FeCl_3 \longrightarrow$ $(RCOO)_3Fe + 3NH_4Cl + 3H_2O$ $\downarrow H_2O$ $Fe(OH)(OOCR)_2 + RCOOH$ Basic iron salt	Red : acetic acid, formic acid No colour change : oxalic acid Violet : salicylic acid Buff : benzoic acid

(F) Detection of amino group

	Primary amines		
(i)	Nitrous acid test	$R-NH_2 + HNO_2 \longrightarrow R-OH + N_2\uparrow + H_2O$	N_2 effervescence indicates 1° amino group.
(ii)	Carbylamine test	$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta}$ $R-N\equiv C + 3KCl + 3H_2O$ Isocyanide	Offensive smell of isocyanide indicates 1° aliphatic or aromatic amino group.
(iii)	Azo dye test	$C_6H_5NH_2 + NaNO_2 + HCl \xrightarrow[\text{5-10 atm}]{\text{0-5°C}} C_6H_5N_2^+Cl^-$ Orange azo dye	A red or orange coloured dye confirms 1° aromatic amino group.

Secondary amines

(i)	Liebermann's nitroso test	$C_6H_5-N-H + HNO_2 \longrightarrow$ $\quad\quad\; \mid$ $\quad\quad CH_3$ $\quad\quad\quad\quad CH_3$ $\quad\quad\quad\quad \mid$ $\quad\quad C_6H_5-N-N=O + H_2O$ Nitrosoamine	Formation of a yellow oily nitrosoamine indicates 2° aliphatic or aromatic amino group.

(G) Detection of nitro group

(i)	Mulliken Barker test	$RNO_2 + 4[H] \xrightarrow{Zn + NH_4Cl} RNHOH + H_2O$ $RNHOH + 2[Ag(NH_3)_2]OH \longrightarrow$ $\quad RNO + 2H_2O + 4NH_3 + 2Ag\downarrow$ Grey black ppt.	Appearance of grey black ppt.
(ii)	Ferrous hydroxide test	$RNO_2 + 6Fe(OH)_2 + 4H_2O \longrightarrow$ Light green $\quad RNH_2 + 6Fe(OH)_3\downarrow$ Brown ppt.	Appearance of brown ppt.

Distinctions

Test	Phenol	Alcohol
Blue litmus test	Turns red	×
$FeCl_3$ test	Gives blue, violet, green or red colouration	×
Azo dye test	Forms orange-red colour dye	×
Br_2-water test	Gives white ppt.	×

Test	Phenol	Carboxylic acid
$NaHCO_3$ test	×	Gives brisk effervescence

Test	Aldehyde	Ketone
Tollens' test	Gives shiny silver mirror	×
Fehling's solution test	Gives red ppt.	×
Schiff's reagent test	Gives pink colour	×
Reduction with $LiAlH_4$	Reduced to 1° alcohol	Reduced to 2° alcohol
Peroxy acid (Caro's acid, peroxy benzoic acid)	Acid is formed.	Ester is formed.

Key Points

- Cerric ammonium test for alcoholic group, is not reliable as many aromatic amines which are easily oxidisable also give this test.
  - Some phenols also react with cerric ammonium nitrate to give green or brown ppt.
- Alcohols on reaction with sodium metal give brisk effervescence due to the evolution of hydrogen gas which burns with 'pop' sound.
  $2ROH + 2Na \longrightarrow 2RONa + H_2\uparrow$
  - This test is not specific for alcohols as phenols and carboxylic acids also give this test.
- Ferric chloride test for phenolic group is not reliable as it is also characteristic of enols $\left[\begin{array}{c} OH \\ | \\ -C=C- \end{array} \right]$.
- Sod. bisulphite test is given by most of the aliphatic aldehydes and methyl ketones which are not sterically hindered such as acetaldehyde, acetone, ethyl methyl ketone.

- Among aromatic aldehydes and ketones, only benzaldehyde gives this test but acetophenone, benzophenone do not give this test.
- Iodoform test is given by only methyl ketones (ketones containing $-COCH_3$ group).
- $NaHCO_3$ test for carboxylic group, is not reliable since some phenols such as 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol (picric acid) also respond to this test.

Preparation of Organic Compounds

- **Acetanilide :** It is an acetyl derivative of aniline.
  - It is prepared by acetylation of aniline.
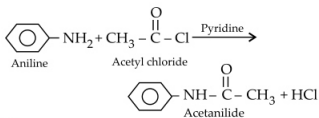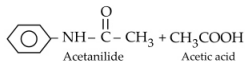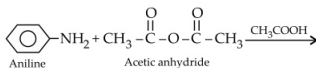
- It is nucleophilic acyl substitution reaction in which aniline acts as nucleophile and acetic anhydride acts as an electrophile.
- **p-Nitroacetanilide :** It is a nitro derivative of acetanilide.
  - It is prepared by nitration of acetanilide with nitrating mixture.
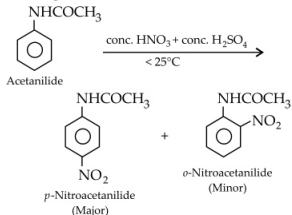
- It is an electrophilic substitution reaction in which acetanilide acts as nucleophile and nitronium ion acts as an electrophile.

- **Aniline yellow :** It is *p*-aminoazobenzene.
  - ○ It is prepared by coupling benzenediazonium chloride with aniline in acidic medium.

$$\text{C}_6\text{H}_5\overset{+}{\text{N}}\equiv\text{NCl}^- + \text{C}_6\text{H}_5-\text{NH}_2 \xrightarrow{\text{H}^+}$$

$$\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{NH}_2 + \text{HCl}$$
    Aniline yellow
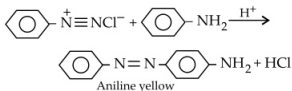
- **Iodoform :** It is triiodomethane. It is used as a mild antiseptic and disinfectant.
  - ○ It is prepared by treating organic compound containing $\text{CH}_3-\overset{\text{OH}}{\underset{|}{\text{CH}}}-$ (ethanol, propan-2-ol, butan-2-ol) or $\text{CH}_3-\overset{\text{O}}{\underset{||}{\text{C}}}-$ (acetone, butan-2-one, acetophenone) with iodine in presence of sodium hydroxide.

$$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[\text{or NaOI}]{\text{KOI}} \text{CH}_3\text{CHO} \quad (\text{Oxidation})$$

$$\text{CH}_3\text{CHO} \xrightarrow[\text{or NaOI}]{\text{KOI}} \text{CI}_3\text{CHO} \quad (\text{Iodination})$$

$$\text{CI}_3\text{CHO} + \text{NaOH} \longrightarrow$$
$$\text{CHI}_3 + \text{HCOONa} \ (\text{Hydrolysis})$$
    Iodoform
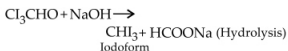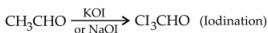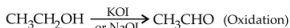
  - ○ With acetone no initial oxidation takes place.

$$\text{CH}_3\text{COCH}_3 \xrightarrow[\text{(Iodination)}]{\text{NaOI}} \text{CI}_3\text{COCH}_3$$

$$\text{CI}_3\text{COCH}_3 + \text{NaOH} \xrightarrow{\text{Hydrolysis}} \text{CHI}_3 \\ + \text{CH}_3\text{COONa}$$
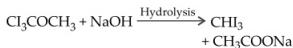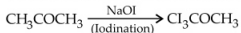
- Introduction
- Titrimetric exercises

Titrimetric Exercises

- It is a method of determining the strength (molarity/normality) or concentration of one solution using another solution of known strength under volumetric conditions.
- Method of finding the volume of one solution which reacts with a definite volume of another solution is known as volumetric analysis.
- **Titration :** It is the process of adding one known solution (standard solution) from the burette to another unknown solution taken in the conical flask till the reaction between the two solutions is complete.

- **Standard solution :** It is a solution of known strength.
  - ○ *Primary standard solutions :* They can be prepared directly by dissolving a known weight of the substance and making a known volume of the solution. *e.g.,* oxalic acid, sodium carbonate, Mohr's salt.
  - ○ *Secondary standard solutions :* They cannot be prepared directly by weighing. *e.g.,* KMnO_4 or hygroscopic substances like NaOH, KOH, or whose concentrations are known only approximately like HCl, H_2SO_4, etc.

- **Titrate :** It is the substance whose concentration is to be determined by titration.

- **Titrant :** It is the solution of known strength (usually taken in the burette).

- **Indicator :** It is the substance which indicates the end point of titration (by change of colour).

- **Equivalence (end) point :** It is the point at which the chemical reaction involved in the titration is just complete.

- **Strength of a solution :** It is the amount of solute in grams present per litre of the solution.
  - ○ Strength (g/L) = Normality × Eq. wt.
  - ○ Strength (g/L) = Molarity × Mol. mass

- **Normality equation :** $\underset{(\text{Solution 1})}{N_1V_1} = \underset{(\text{Solution 2})}{N_2V_2}$

- **Molarity equation :** $\underset{(\text{Solution 1})}{M_1V_1n_1} = \underset{(\text{Solution 2})}{M_2V_2n_2}$

  $[\because N = M \times n, \text{ where } n = \text{valency factor}]$

- **Percentage purity of a given salt**

$$= \frac{\text{Strength of pure sample}}{\text{Strength of given sample}} \times 100$$

Types of Titrations

- **Acid-base titrations :** In acid-base titration, the amount of an acid or base is determined by titrating it against a standard solution of base or acid respectively. It involves neutralisation reaction.

$$\underset{\text{From acid}}{\text{H}^+} + \underset{\text{From base}}{\text{OH}^-} \longrightarrow \underset{\text{Water}}{\text{H}_2\text{O}}$$

  - ○ *Choice of indicators :* The choice of an indicator should be made in such a way that indicator used shows change in colour in the same pH range as developed around the equivalence point.

    e.g. Phenolphthalein : $\underset{\text{Colourless}}{\text{HPh}} \rightleftharpoons \text{H}^+ + \underset{\text{Pink}}{\text{Ph}^-}$

    Methyl orange : $\underset{\text{Yellow}}{\text{MeOH}} \rightleftharpoons \text{Me}^+ + \underset{\text{Red}}{\text{OH}^-}$

Acid	Alkali	Indicator	End point
Strong acid (HCl, H_2SO_4, HNO_3)	Strong alkali (NaOH, KOH)	Phenolphthalein or methyl orange	Pink to colourless or yellow/orange to red, vice versa
Weak acid (oxalic acid, acetic acid)	Strong alkali (NaOH, KOH)	Phenolphthalein	Pink to colourless, vice versa
Strong acid (HCl, H_2SO_4, HNO_3)	Weak alkali (Na_2CO_3, $NaHCO_3$, $KHCO_3$, NH_4OH)	Methyl orange	Yellow/orange to red, vice versa

❑ **Redox titrations :** These titrations proceed with transfer of electrons among the reacting ions in aqueous solutions.

　❍ **Titration of oxalic acid vs KMnO$_4$**

　　– $2KMnO_4 + 3H_2SO_4 + 5\left|\begin{array}{c}COOH\\COOH\end{array}\cdot 2H_2O\longrightarrow$

　　　$K_2SO_4 + 2MnSO_4 + 18H_2O + 10CO_2$
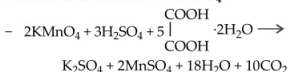
　　– **Calculations**

$$\frac{M_{KMnO_4} \times V_{KMnO_4}}{M_{oxalic\ acid} \times V_{oxalic\ acid}} = \frac{2}{5}$$

　❍ **Titration of Mohr's salt vs KMnO$_4$**

　　– $2KMnO_4 + 8H_2SO_4 +$
　　　$10FeSO_4\cdot(NH_4)_2SO_4\cdot6H_2O\longrightarrow$
　　　　$K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 +$
　　　　　$10(NH_4)_2SO_4 + 68H_2O$
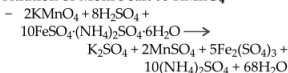
　　– **Calculations**

$$\frac{M_{KMnO_4} \times V_{KMnO_4}}{M_{Mohr's\ salt} \times V_{Mohr's\ salt}} = \frac{1}{5}$$

Physical Chemistry Experiments

❑ **Enthalpy of solution of CuSO$_4$**

　❍ It is the amount of heat change involved during the dissolution of one mole of a solute in such a large excess of solvent so that no further heat changes occur on dilution.
　　$CuSO_{4(s)} + H_2O \longrightarrow CuSO_{4(aq)}$
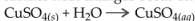
　❍ Dissolution of $CuSO_{4(s)}$ in water is exothermic. The enthalpy of solution of $CuSO_{4(s)}$ is calculated from the highest temperature attained during its dissolution.

　❍ **Calculations :** If dissolution of w g of $CuSO_4$ in 200 g solvent (water) causes $\Delta t°C$ change in temperature, then
　　Heat evolved (q) = Mass × Specific heat × Change in temperature
　　　$q = 200 \times 4.2 \times \Delta t$　J
　　Enthalpy of solution of $CuSO_4$ in water
　　$= \dfrac{-q \times 159.5 \times 10^{-3}}{w}$ kJ

❑ **Enthalpy of neutralisation of strong acid and strong base**

　❍ It is the enthalpy change accompanying neutralisation of one gram equivalent of a base by an acid in dilute solutions at a given temperature.
　　$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$
　　It is an exothermic reaction.
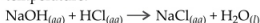
　❍ The heat of neutralisation of a strong acid by a strong base in their dilute solutions is generally 57.3 kJ. The reaction may be represented as
　　$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O$, $\Delta H = -57.3$ kJ.

　❍ **Calculations :** Heat evolved during neutralisation of 100 mL of 0.5 N HCl,
　　$q = (200 + w) \times \Delta t \times 4.2$ J, where w is water equivalent of calorimeter (given).
　　Thus, enthalpy of neutralisation of 1000 mL of 1 N HCl and NaOH $= \dfrac{-q}{0.5 \times 100}$ kJ

Preparation of Sols

❑ A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance (dispersion medium).

　❍ **Lyophilic colloids :** The colloidal solutions in which the dispersed phase have great affinity (or love) for the dispersion medium are called lyophilic colloids.

　❍ **Lyophobic colloids :** The colloidal solution in which the particles of the dispersed phase have no affinity (or love) for the dispersion medium are called lyophobic colloids.

　　– Such solutions are formed with difficulty and are unstable and are stabilised by the addition of a small amount of electrolytes, also called stabilizers.

　　– In case the dispersion medium is water, the lyophobic colloids are called hydrophobic colloids.

❑ **Preparation of lyophilic sols :** These sols are prepared by shaking the lyophilic material with

the dispersion medium. *e.g.* colloidal sols of gelatin, gum, starch, egg albumin, etc.

❑ **Preparation of lyophobic sols :** Colloidal sols of ferric hydroxide and aluminium hydroxide can be prepared by hydrolysis of $FeCl_3$ and $AlCl_3$ with distilled water. HCl produced, is removed with dialysis.

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$
<div align="center">Red or brown sol</div>
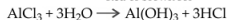
$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$
<div align="center">Colourless sol</div>

Kinetic Study of Reaction of Iodide Ion with Hydrogen Peroxide at Room Temperature

❑ Hydrogen peroxide oxidises iodide ion (from KI) to iodine in acidic medium.

$$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \longrightarrow I_{2(aq)} + 2H_2O_{(l)}$$
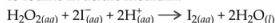
○ When this reaction is carried out in presence of a small amount of sodium thiosulphate and starch, the iodine produced first reacts with sodium thiosulphate as follows:

$$2S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} \longrightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-_{(aq)}$$
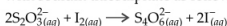
○ When thiosulphate ions get completely consumed, the liberated iodine reacts with starch solution to give blue coloured complex.

$$I_{2(aq)} + starch_{(aq)} \longrightarrow Blue\ complex$$

As the concentration of thiosulphate ion is kept constant, the different time taken (t_c) for the appearance of blue colour with change in concentration of either reactant indicates the relative rate of reaction.

$$Initial\ rate \propto \frac{1}{t_c}$$

○ The rate of reaction decreases with decrease in concentration of KI.

○ The graph of $1/t_c$ versus volume of KI solution is a straight line.

○ Rate of reaction ∝ Concentration of KI

○ Similarly, by keeping I^- ion concentration constant and taking different concentrations of H_2O_2, the rate w.r.t. H_2O_2 can be found out.

Questions for Practice

1. A student was given 2 mL of solutions *A* and *B* separately. She added aqueous solution of $NaHCO_3$ in both the solutions and then she treated both solutions with neutral ferric chloride solution. Observations are recorded in the given table.

Solutions	NaHCO$_3$ test	FeCl$_3$ test
A	No reaction	Violet colouration
B	Brisk effervescence	Red colouration

Solutions *A* and *B* are respectively
(a) acetic acid and phenol
(b) phenol and oxalic acid
(c) formic acid and phenol
(d) phenol and acetic acid.

2. Lassaigne's test for which of the following organic compounds is positive?
(a) Hydrazine   (b) Hydroxylamine
(c) Urea   (d) Both (a) and (b)

3. Which of the following radicals gives brown ppt. with Nesseler's reagent?
(a) S^{2-} (b) Ni^{2+}
(c) NH_4^+ (d) CH_3COO^-

4. Radical that gives rosy red ppt. with DMG is
(a) Cd^{2+} (b) Ni^{2+}
(c) Mn^{2+} (d) Ba^{2+}

5. In the study of oxidation of I^- ions by H_2O_2 in presence of dilute H_2SO_4, and starch as a clock reaction, if excess of thiosulphate is added
(a) blue colour will appear immediately
(b) blue colour will appear very late
(c) blue colour will not appear at all
(d) heating will be required to obtain blue colour.

6. Which of the following gives colourless, odourless gas which burns with blue flame and turns lime-water milky when treated with conc. H_2SO_4?
(a) $C_2O_4^{2-}$ (b) CO_3^{2-}
(c) SO_3^{2-} (d) SO_4^{2-}

7. In Lassaigne's test, organic compound is fused with a piece of sodium metal so as to
(a) convert the covalent compound into a mixture of ionic compounds
(b) decrease the melting point of the compound
(c) increase the reactivity of the compound
(d) increase the ionization of the compound.

8. The compound formed in borax bead test is
(a) orthoborate   (b) tetraborate
(c) boric acid   (d) metaborate.

9. Before testing for halogens, the Lassaigne's extract is boiled with

(a) conc. HCl   (b) NaOH
(c) conc. HNO$_3$ (d) Any of these.

10. Which of the following radicals gives waxy gelatinous white solid on treating with sand and conc. H$_2$SO$_4$?
(a) BO$_3^{3-}$ (b) F$^-$
(c) CH$_3$COO$^-$ (d) C$_2$O$_4^{2-}$

11. Which of the following reagents is used for the separation of acetaldehyde from acetophenone?
(a) NH$_2$OH   (b) NaOH + I$_2$
(c) NaHSO$_3$ (d) C$_6$H$_5$NHNH$_2$

12. Which of the following organic compounds gives blood red colour while performing Lassaigne's test for nitrogen?
(a) (NH$_2$)$_2$CS   (b) (NH$_2$)$_2$CO
(c) Na$_2$SO$_3$ (d) Na$_2$CO$_3$

13. A violet colour with sodium nitroprusside in the test of sulphur in organic compound is due to the formation of
(a) Na$_2$[Fe(CN)$_5$S]   (b) Na$_4$[Fe(CN)$_5$NOS]
(c) Na$_2$[Fe(NO)(CN)$_5$]   (d) Na$_3$[Fe(CN)$_6$]

14. Match the list I with list II and select the correct answer using the code given below the lists.

	List I		List II
P.	Sr^{2+}	1.	Golden yellow
Q.	K$^+$	2.	Apple green
R.	Na$^+$	3.	Crimson red
S.	Ba^{2+}	4.	Lilac

	P	Q	R	S
(a)	1	2	3	4
(b)	3	4	1	2
(c)	2	1	4	3
(d)	4	3	1	2

15. An unknown compound 'A' C$_8$H$_6$O$_5$, on methylation forms a methyl derivative whose molecular weight is 210. The number of –OH groups in 'A' is
(a) 1   (b) 2
(c) 4   (d) 5

16. In the titration of Mohr's salt *vs* potassium permanganate, indicator used and the point of inflection is
(a) phenolphthalein, colourless to light pink
(b) methyl orange, red to yellow
(c) methyl red, orange to yellow
(d) potassium permanganate, colourless to light pink.

17. Identify the incorrect statement.
(a) 1 mole of KMnO$_4$ reacts with 2.5 moles of oxalic acid.

(b) 1 mole of KMnO$_4$ reacts with 5 moles of Mohr's salt.
(c) 1 mole of oxalic acid reacts with 0.4 moles of KMnO$_4$.
(d) 1 mole of Mohr's salt reacts with 0.5 moles of KMnO$_4$.

18. Choose the correct statement.
(a) Dissolution of both anhydrous and hydrated copper sulphate in water is exothermic.
(b) Dissolution of both anhydrous and hydrated copper sulphate in water is endothermic.
(c) Dissolution of anhydrous copper sulphate in water is exothermic but dissolution of hydrated copper sulphate in water is endothermic.
(d) Dissolution of anhydrous copper sulphate in water is endothermic but dissolution of hydrated copper sulphate in water is exothermic.

19. In qualitative analysis NH$_4$Cl is added before NH$_4$OH
(a) to decrease [OH$^-$]
(b) to increase [OH$^-$]
(c) for making HCl
(d) all the statements are wrong.

20. Which of the following cannot be used as starting material for the preparation of iodoform?
(a) Butan-2-one   (b) Acetophenone
(c) Propan-2-ol   (d) Propan-1-ol

21. Aniline yellow is
(a) *p*-nitroazobenzene
(b) *p*-aminoazobenzene
(c) *p*-hydroxyazobenzene
(d) *p*-nitrosoazobenzene.

22. The total number of ions produced when Mohr's salt is dissolved in water is
(a) 4   (b) 5
(c) 3   (d) 8

23. Match the list I with list II and select the correct answer using the code given below the lists.

	List I		List II
P.	Phthalein test	1.	Aldehydic group
Q.	Schiff's reagent test	2.	Amino group
R.	Nitrous acid test	3.	Alcoholic group
S.	Xanthate test	4.	Phenolic group

	P	Q	R	S
(a)	1	2	3	4
(b)	4	3	2	1
(c)	1	3	2	4
(d)	4	1	2	3

24. Salt which does not respond to dilute and concentrated sulphuric acid is
(a) Na_2SO_4 (b) Na_3PO_4
(c) CaF_2 (d) All of these.

25. If $H^+ + OH^- \rightarrow H_2O + 13.7$ kcal, then heat of complete neutralisation of one gram mole of H_2SO_4 with a base will be
(a) 13.7 kcal (b) 27.4 kcal
(c) 6.85 kcal (d) 3.425 kcal

26. To determine the enthalpy of neutralisation of HCl with NaOH, we use
(a) 0.2 N HCl, 0.2 N NaOH
(b) 0.5 N HCl, 0.5 N NaOH
(c) 1 N HCl, 1 N NaOH
(d) any of these.

27. Enthalpy of neutralisation of H_2SO_4 with NaOH is
(a) same as that of HCl with NaOH
(b) double than that of HCl with NaOH
(c) half than that of HCl with NaOH
(d) double than that of HNO_3 with NaOH.

28. When CS_2 layer containing both Br_2 and I_2 is shaken with excess of Cl_2 water, the violet colour due to I_2 disappears and orange colour due to Br_2 appears. The disappearance of violet colour is due to the formation of
(a) I_3^- (b) HIO_3
(c) ICl_2 (d) I^-

29. H_2S in the presence of HCl precipitate group II but not group IV because
(a) HCl activates H_2S
(b) HCl increases concentration of Cl^-
(c) HCl decreases concentration of S^{2-}
(d) HCl lowers the solubility of H_2S in solution.

30. Acidified $KMnO_4$ oxidizes oxalic acid to CO_2. What is the volume of 10^{-4} M $KMnO_4$ required to completely oxidize 0.5 litre of 10^{-2} M oxalic acid in acid medium?
(a) 125 L (b) 1250 L
(c) 200 L (d) 20 L

SOLUTIONS

1. **(d) :** Phenol does not respond to $NaHCO_3$ test and gives violet colour with $FeCl_3$.
Acetic acid gives brisk effervescence with $NaHCO_3$ and red colour on treating with $FeCl_3$.

2. **(c) :** For positive Lassaigne's test of nitrogen, an organic compound must contain carbon along with nitrogen.

3. **(c) :** With Nesseler's reagent, ammonium salts form a brown precipitate.

$$NH_3 + \underset{\text{Pot. tetraiodomercurate(II)}}{2K_2[HgI_4]} + 3KOH$$

$$\underset{\substack{\text{Iodide of Millon's base} \\ \text{(Brown ppt.)}}}{H_2NHgO\cdot HgI} + 7KI + 2H_2O$$
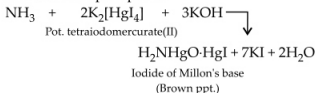
4. **(b) :** Ni^{2+} in presence of ammonia gives rosy red ppt. of bis(dimethylglyoximato)nickel(II) complex.

$$NiCl_2 + 2NH_4OH + 2 \underset{\text{Dimethylglyoxime}}{\begin{array}{c}CH_3 - C = NOH \\ CH_3 - C = NOH\end{array}}$$

Bright red complex (ppt.)

$$+ 2NH_4Cl + 2H_2O$$
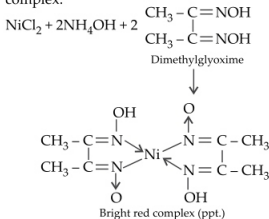
5. **(c) :** In the presence of excess of thiosulphate, whole of iodine liberated from the main reaction will react with it and no blue colour will be obtained.

6. **(a) :** Salt of oxalate on treatment with conc. H_2SO_4 liberates colourless, odourless gas which burns with blue flame and turns limewater milky.
$$Na_2C_2O_4 + H_2SO_4 \rightarrow Na_2SO_4 + H_2C_2O_4$$
$$H_2C_2O_4 + [H_2SO_4] \rightarrow$$
$$\underset{\substack{\text{burns with} \\ \text{blue flame}}}{CO} + \underset{\substack{\text{turns lime-} \\ \text{water milky}}}{CO_2} + H_2O + [H_2SO_4]$$

7. **(a) :** This is done to get a mixture of ionic compounds such as NaCN, Na_2S, NaX, etc.

8. **(d)**

9. **(c) :** Lassaigne's extract is boiled with conc. HNO_3 to decompose Na_2S and NaCN which would otherwise interfere with the tests of halogens. HCl cannot be used because we cannot add Cl^- ion when we have to test for Cl in the organic compound. NaOH also cannot be used because it would precipitate $AgNO_3$ as AgOH.

10. **(b) :** $\underset{\text{Salt}}{2NaF} + H_2SO_4 \longrightarrow Na_2SO_4 + \underset{\text{Hydrofluoric acid}}{H_2F_2}$

$$\underset{\text{Silica}}{SiO_2} + 2H_2F_2 \longrightarrow \underset{\substack{\text{Silicon} \\ \text{tetrafluoride}}}{SiF_4} + 2H_2O$$

$$3SiF_4 + 4H_2O \longrightarrow \underset{\substack{\text{Silicic acid} \\ \text{(Gelatinous white)}}}{H_4SiO_4} + 2H_2SiF_6$$

11. **(c)** : Acetaldehyde gives white ppt. with $NaHSO_3$ while acetophenone will not give white ppt. with $NaHSO_3$ due to steric hindrance.

12. **(a)** : An organic compound containing C, N and S will give blood red colour while performing Lassaigne's test for nitrogen.

$$Na + C + N + S \xrightarrow{\Delta} \underset{\substack{\text{(Sodium thiocyanate)} \\ \text{(Lassaigne's extract)}}}{NaSCN}$$

$$NaSCN + FeCl_3 \longrightarrow \underset{\text{Blood red}}{[Fe(SCN)]Cl_2 + NaCl}$$

13. **(b)** : $\underset{\text{Sodium nitroprusside}}{Na_2S + Na_2[Fe(CN)_5NO]} \to \underset{\text{Violet}}{Na_4[Fe(CN)_5NOS]}$

14. **(b)**

15. **(b)** : The change in molar mass = 210 − 182 = 28. Two hydrogens are replaced by two methyl groups carry a group mass of 30. Hence there are two hydroxyl groups present.

16. **(d)** : Potassium permanganate, $KMnO_4$ acts as a self indicator and point of inflection is the colourless to permanent light pink.

17. **(d)** : $2KMnO_4 + 3H_2SO_4 + 5\,\underset{\text{COOH}}{\overset{\text{COOH}}{|}}\cdot 2H_2O \longrightarrow$

$$K_2SO_4 + 2MnSO_4 + 18H_2O + 10CO_2$$

It is obvious from the equation that 2 moles of $KMnO_4$ react with 5 moles of oxalic acid. Thus 1 mole of $KMnO_4$ will react with 2.5 moles of oxalic acid.

$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

$\longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3$
$\qquad\qquad + 10(NH_4)_2SO_4 + 68H_2O$

It is obvious from above equation that 10 moles of Mohr's salt will react with 2 moles of $KMnO_4$.

Thus 1 mole of Mohr's salt will react with $\dfrac{2}{10} = \dfrac{1}{5}$ mole of $KMnO_4$.

18. **(c)**

19. **(a)** : NH_4Cl decreases OH^- concentration due to common ion effect.

20. **(d)** : Organic compound having either $\underset{\substack{|\\CH_3-CH-}}{OH}$ group or $\underset{\substack{\|\\CH_3-C-}}{O}$ group is used for the preparation of iodoform. Propan-1-ol, $CH_3CH_2CH_2OH$ does not contain such groups.

21. **(b)** :

$$\underset{\substack{\text{p-Aminoazobenzene} \\ \text{(Aniline yellow)}}}{\bigcirc - N = N - \bigcirc - NH_2}$$

22. **(b)** : $FeSO_4.(NH_4)_2SO_4 \cdot 6H_2O \longrightarrow$

$$\underbrace{Fe^{2+} + 2NH_4^+ + 2SO_4^{2-}}_{\text{Total 5 ions}} + 6H_2O$$

23. **(d)**

24. **(d)** : Salts of sulphate, phosphate, fluoride and borate do not respond to dilute and concentrated sulphuric acids.

25. **(d)** : H_2SO_4 is a dibasic acid. One gram mole of H_2SO_4 produces two gram moles of H^+ ions.
$$H_2SO_4 \to 2H^+ + SO_4^{2-}$$
Thus neutralisation reaction will be
$$2H^+ + 2OH^- \to 2H_2O + (13.7 \times 2) \text{ kcal}$$
Hence heat of neutralisation = 13.7 × 2 = 27.4 kcal

26. **(d)** : As in every case, normalities of HCl and NaOH are equal, any of the given pair of acid and base can be used.

27. **(a)** : H_2SO_4 and NaOH are strong acid and strong base. HCl and NaOH are also strong acid and strong base. Hence, their enthalpies of neutralisation are same.

28. **(b)** : $\underset{\text{excess}}{5Cl_2} + I_2 + 6H_2O \to \underset{\text{Colourless}}{2HIO_3} + 10HCl$

29. **(c)** : Due to common ion effect, HCl decreases concentration of S^{2-} ions and only group II basic radicals are precipitated.

30. **(d)** : $2KMnO_4 + 3H_2SO_4 + 5\,\underset{\text{COOH}}{\overset{\text{COOH}}{|}} \longrightarrow$

$$K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

$$\frac{M_1V_1}{2}(KMnO_4) = \frac{M_2V_2}{5}\left(\underset{\text{COOH}}{\overset{\text{COOH}}{|}}\right)$$

$$\frac{10^{-4} \times V_1}{2} = \frac{10^{-2} \times 0.5}{5}$$

$$V_1 = 20 \text{ L}$$

CONCEPT MAP

THE SOLID STATE

Classification

Amorphous Solid

- Constituent particles are not arranged in any regular pattern.
- Short range ordered
- Isotropic
- Supercooled liquids or pseudo solids

Crystalline Solid

- Constituent particles are arranged in a definite geometric pattern in all the three dimensions.
- Short range as well as long range ordered
- Anisotropic
- True solids
- On the basis of nature of intermolecular forces between them there are four types of crystalline solids:
  - Molecular solids
  - Ionic solids : Non-polar, Polar, Hydrogen bonded
  - Metallic solids
  - Covalent solids

Crystal/Space Lattice and Unit Cell

Primitive/Simple Unit Cell

- Constituent particles are present only at the corners of the unit cells.
- These are of 7 types of which cubic is most symmetric and triclinic is least symmetric.

Non-primitive/Centred Unit Cell

- Constituent particles are present not only at the corners but also at some other positions.
- These are of 3 types.
- In addition to the particles at the corners of the unit cell
  - Body-centred : also present at the centre of the unit cell.
  - Face-centred : also present at the centre of each face of the unit cell. (Most efficient packing)
  - End-centred : also present at the centre of any two opposite faces.

Cubic System

$$d = \frac{Z \times M}{a^3 \times N_A} \text{ g cm}^{-3}$$

Total No. of Atoms Per Unit Cell

Simple cubic	bcc	fcc
$8 \times \frac{1}{8} = 1$	$8 \times \frac{1}{8} + 1 \times 1 = 2$	$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

Relation between d, a and r

Simple cubic	$r = \frac{d}{2} = \frac{a}{2}$ since $d = a$
fcc	$r = \frac{d}{2} = \frac{a}{2\sqrt{2}}$ since $d = \frac{a}{\sqrt{2}}$
bcc	$r = \frac{d}{2} = \frac{\sqrt{3}a}{4}$ since $d = \frac{\sqrt{3}a}{2}$

Coordination Number and Packing Efficiency

Type	Simple cubic	bcc	fcc
Coordination number	6	8	12
Packing efficiency	52.4%	68%	74%

Size and No. of Voids

Type	Size	No. of Voids
Octahedral	0.414 R	N
Tetrahedral	0.225 R	2N

Defects

Line Defects

Irregularities exist in the entire row of lattice points.

Point Defects

Irregularities exist around a point or an atom.

Stoichiometric defects (Intrinsic or thermodynamic defects)

- Vacancy defect : Non-ionic solids
  - Arises when some of the lattice sites are vacant.
  - Results in decrease in density of the substance.
- Interstitial defect : Non-ionic solids
  - Arises when some constituent particles occupy an interstitial site.
  - Results in increase in density of the substance.
- Frenkel defect : Ionic solids
  - Arises due to delocalization of smaller ion (usually cation) from its normal site to an interstitial site.
  - Results in vacancy defect. Also called as dislocation defect.
  - Does not affect the density of the substance.
- Schottky defect : Ionic solids
  - Characterized by missing of equal number of cations and anions from their lattice site to maintain electrical neutrality.
  - Results in vacancy defect and decrease in density of the substance.

Impurity defects

Arises when foreign atoms are present at the lattice site in place of host atoms (substitutional solid solutions) or at the vacant interstitial sites (interstitial solid solutions).

Non-Stoichiometric defects

Metal excess defect
- Metal excess defect arises due to anionic vacancies.
  - Leaving a hole which is occupied by an electron thus maintaining electrical balance. These are called F-centres and impart colour to crystals.
  - Similar to Schottky defects.
- Metal excess defect arises due to presence of extra cations at interstitial sites.
  - Electrical neutrality is maintained by an electron present in another interstitial site.
  - Similar to Frenkel defects.
Metal deficiency defect
- Metal deficiency defect arises when metal shows variable valency i.e., in transition metals.
  - The defect occurs due to missing of a cation from its lattice site and the presence of the cation having high charge in the adjacent lattice site.

Properties

Electrical Properties

Solids may be classified into three categories depending upon their values of electrical conductivity.
- Conductors : Electrical conductivity, 10^4 to 10^7 ohm^{-1} m^{-1}
- Insulators : Electrical conductivity, 10^{-20} to 10^{-10} ohm^{-1} m^{-1}
- Semiconductors : Electrical conductivity, 10^{-6} to 10^4 ohm^{-1} m^{-1}
  - n-type semiconductors : Group 14 elements doped with group 15 elements, free electrons increase conductivity.
  - p-type semiconductors : Group 14 elements doped with group 13 elements, holes increase conductivity.

Magnetic Properties

Solid substances are classified into following categories depending upon their behaviour towards magnetic field.
- Diamagnetic Substances : Substances which are weakly repelled by external magnetic field. e.g. N_2, NaCl, Zn, TiO_2, etc.
- Paramagnetic Substances : Substances which are weakly attracted by external magnetic field. e.g. O_2, Cu^{2+}, Fe^{3+}, etc.
- Ferromagnetic Substances : Substances which show permanent magnetism even in the absence of external magnetic field. e.g. Ni, Fe, Co, etc.
- Antiferromagnetic Substances : Substances which have zero net dipole moment even though they are having large number of unpaired electrons. e.g. MnO.
- Ferrimagnetic Substances : These are the substances which possess very small net magnetic moment even though they are having a large number of unpaired electrons. e.g. Fe_3O_4.
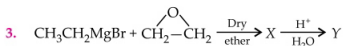
NCERT CORNER

CLASS XI-XII

1. In the reaction:

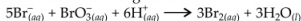$$3Br_2 + 6CO_3^{2-} + 3H_2O \longrightarrow 5Br^- + BrO_3^- + 6HCO_3^-$$

(a) bromine is oxidized and carbonate is reduced

(b) bromine is reduced and water is oxidized

(c) bromine is neither reduced nor oxidized

(d) bromine is both reduced and oxidized.

2. If the shortest wavelength of H-atom in Lyman series is x. Then, longest wavelength in Balmer series of He^+ is

(a) $\dfrac{9x}{5}$ (b) $\dfrac{36x}{5}$

(c) $\dfrac{x}{5}$ (d) $\dfrac{5x}{9}$

3. $CH_3CH_2MgBr + CH_2\!-\!CH_2 \xrightarrow[\text{ether}]{\text{Dry}} X \xrightarrow[\text{H}_2\text{O}]{\text{H}^+} Y$

Final product Y in the above reaction is

(a) butan-2-ol (b) propan-1-ol

(c) butan-1-ol (d) propan-2-ol.

4. Which of the following expressions is correct for the rate of reaction given below?

$$5Br^-_{(aq)} + BrO^-_{3(aq)} + 6H^+_{(aq)} \longrightarrow 3Br_{2(aq)} + 3H_2O_{(l)}$$

(a) $\dfrac{\Delta[Br^-]}{\Delta t} = 5\dfrac{\Delta[H^+]}{\Delta t}$ (b) $\dfrac{\Delta[Br^-]}{\Delta t} = \dfrac{6}{5}\dfrac{\Delta[H^+]}{\Delta t}$

(c) $\dfrac{\Delta[Br^-]}{\Delta t} = \dfrac{5}{6}\dfrac{\Delta[H^+]}{\Delta t}$ (d) $\dfrac{\Delta[Br^-]}{\Delta t} = 6\dfrac{\Delta[H^+]}{\Delta t}$

5. Which of the following represents the negative overlap?
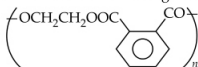
(a)

(b)

(c)

(d)
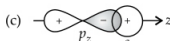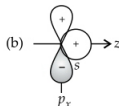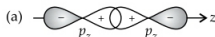
6. Phenol on distillation with zinc dust gives

(a) BHC (b) toluene

(c) benzene (d) chlorobenzene.

7. Molecular formula of inorganic benzene is

(a) C_6H_6 (b) B_6N_6

(c) $B_3N_3H_6$ (d) C_6Cl_6

**8.** The correct IUPAC nomenclature for the following alcohol is
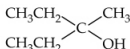
(a) 2-ethylbutan-2-ol

(b) 3-methylpentan-3-ol

(c) 3-ethyl-3-methylpentan-2-ol

(d) 1,1-dimethylbutanol.

9. The monomeric units of the given polymer are

(a) ethylene glycol, terephthalic acid

(b) ethylene glycol, phthalic acid

(c) glycine, phthalic acid

(d) glycine, terephthalic acid.

10. Maltose is made up of

(a) α-D-glucose (b) β-D-glucose

(c) α- and β-D-glucose (d) fructose.

11. Identify P.

(a) Benzophenone   (b) Chlorobenzene
(c) Benzal chloride   (d) Benzaldehyde

12. Which of the following is an antibiotic?
   (a) Insulin   (b) Albumin
   (c) Penicillin   (d) Ascorbic acid

13. A compound P on treatment with Br_2 and KOH, gives an amine Q which gives carbylamine test. Q upon diazotization and coupling with phenol gives an azo dye. P can be
   (a) $C_6H_5CONHCOCH_3$
   (b) $C_6H_5CONH_2$
   (c) $C_6H_5NO_2$
   (d) o-, m- or p-$C_6H_4(NH_2)CHO$

14. Molar conductances of $BaCl_2$, H_2SO_4 and HCl at infinite dilutions are x_1, x_2 and x_3, respectively. Equivalent conductance of $BaSO_4$ at infinite dilution will be
   (a) $\dfrac{(x_1 + x_2 - x_3)}{2}$ (b) $\dfrac{(x_1 - x_2 - x_3)}{2}$
   (c) $2(x_1 + x_2 - 2x_3)$ (d) $\dfrac{(x_1 + x_2 - 2x_3)}{2}$

15. Half-life for a first order reaction is
$$R \longrightarrow P$$
   (a) $\dfrac{[R]_0}{2k}$ (b) $\dfrac{0.693}{k}$
   (c) $\dfrac{\ln 2}{k}$ (d) Both (b) and (c)

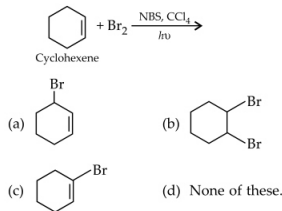16. Which of the following curves is in accordance with Freundlich adsorption isotherm?
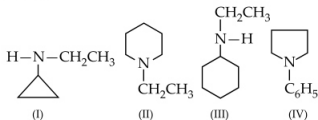

17. The volumes of gas X and gas Y diffusing during the same time are 35 mL and 29 mL respectively. If the molecular weight of gas Y is 71, the molecular weight of gas X is
   (a) 48.7   (b) 56.7
   (c) 52.3   (d) 46.8

18. If pH = 7.4, K_1 of H_2CO_3 = 4.5×10^{-7}, then what will be the ratio of $[HCO_3^-]$ to $[H_2CO_3]$?
   (a) 10.5   (b) 13.5
   (c) 9.6   (d) 11.3

19. Which of the following compounds of xenon has pyramidal geometry?
   (a) $XeOF_4$ (b) XeO_3
   (c) XeF_2 (d) XeF_4

20. Arrange the following compounds in increasing order of their acidic strength:
   m-Nitrophenol m-Cresol
     (I)   (II)
     Phenol m-Chlorophenol
     (III)   (IV)
   (a) (I) < (II) < (III) < (IV)
   (b) (II) < (III) < (I) < (IV)
   (c) (IV) < (III) < (II) < (I)
   (d) (II) < (III) < (IV) < (I)

21. Ozone hole refers to
   (a) hole formed in troposphere from which ozone oozes out
   (b) reduction in thickness of ozone layer in troposphere
   (c) reduction in thickness of ozone layer in stratosphere
   (d) increase in concentration of ozone.

22. For an ideal solution with $p_A > p_B$, which of the following is true?
   (a) $(x_A)_{\text{liquid}} = (x_A)_{\text{vapour}}$
   (b) $(x_A)_{\text{liquid}} > (x_A)_{\text{vapour}}$
   (c) $(x_A)_{\text{liquid}} < (x_A)_{\text{vapour}}$
   (d) $(x_A)_{\text{liquid}}$ and $(x_A)_{\text{vapour}}$ do not bear any relationship with each other.

23. In the reaction :
$S + 3/2\ O_2 \longrightarrow SO_3 + 2x$ kcal and
$SO_2 + 1/2\ O_2 \longrightarrow SO_3 + y$ kcal,
heat of formation of SO_2 is
   (a) $(x + y)$ (b) $(x - y)$
   (c) $(2x + y)$ (d) $(2x - y)$

24. $CH_3 \text{—}$ $\text{—}CH_2CH_3 \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} X$

X in the above reaction is

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25. What will be the final product of the given reaction?

Cyclohexene + Br_2 $\xrightarrow{\text{NBS, CCl}_4 \atop h\upsilon}$

(a)

(b)

(c)

(d) None of these.

26. Which of the following compounds is tertiary amine?

$H-N-CH_2CH_3$ (I)

 (II)

 (III)

 (IV)

(a) (I) and (III) only
(b) (II) and (III) only
(c) (II) and (IV) only
(d) (I), (II) and (IV) only

27. In the periodic table, metallic character of the elements
(a) decreases down the group and increases across the period
(b) increases down the group and decreases across the period
(c) increases across the period and also down the group
(d) decreases down the group and remains constant across the period.

28. The correct order of solubility of the sulphates of alkaline earth metals in water is
(a) Be > Ca > Mg > Ba > Sr
(b) Mg > Be > Ba > Ca > Sr
(c) Be > Mg > Ca > Sr > Ba
(d) Mg > Ca > Ba > Be > Sr

29. Which of the following equations depicts reducing nature of H_2O_2?
(a) $2[Fe(CN)_6]^{4-} + 2H^+ + H_2O_2 \longrightarrow$
$\qquad\qquad 2[Fe(CN)_6]^{3-} + 2H_2O$
(b) $I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$
(c) $Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$
(d) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$
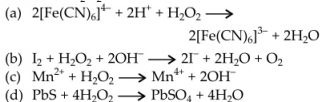
30. Which one of the following statements is incorrect in relation to ionization enthalpy?
(a) Ionization enthalpy increases for each successive electron.
(b) The greatest increase in ionization enthalpy is experienced on removal of electrons from core having noble gas configuration.
(c) End of valence electrons is marked by a big jump in ionization enthalpy.
(d) Removal of electron from orbitals bearing lower n value is easier than from orbital having higher n value.

31. On the basis of following
$PbO_2 \rightarrow PbO, \qquad \Delta G_{298\ K} < 0$
$SnO_2 \rightarrow SnO, \qquad \Delta G_{298\ K} > 0$
most probable oxidation state of Pb and Sn will be
(a) Pb^{4+}, Sn^{4+}
(b) Pb^{4+}, Sn^{2+}
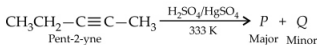(c) Pb^{2+}, Sn^{2+}
(d) Pb^{2+}, Sn^{4+}

32. In a compound, oxide ions have ccp arrangement. The cations A are present in one-eighth of the tetrahedral holes and cations B occupy half the octahedral holes. The simplest formula of the compound is
(a) AB_2O_4
(b) A_2BO_4
(c) ABO_2
(d) ABO_4

33. The atomic weights of two elements A and B are 40 and 80 respectively. If x g of A contains y atoms, how many atoms are present in $2x$ g of B?
(a) $\dfrac{y}{2}$
(b) $\dfrac{y}{4}$
(c) y
(d) $2y$

34. Identify P and Q in the following reaction:

$CH_3CH_2-C\equiv C-CH_3$ $\xrightarrow{H_2SO_4/HgSO_4 \atop 333\ K}$ $\underset{\text{Major}}{P}$ + $\underset{\text{Minor}}{Q}$
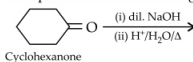Pent-2-yne

(a) Pentan-2-one, Pentan-3-one
(b) Pentan-3-one, Pentan-2-one
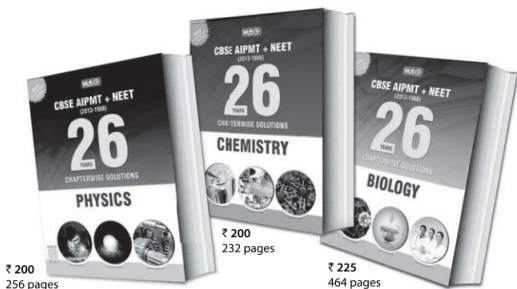(c) Pentan-1-al, Pentan-2-one
(d) Pentan-2-one, Pentan-1-al

35. The oxidation number of S in the compound $KAl(SO_4)_2 \cdot 12H_2O$ is
(a) + 4
(b) + 2
(c) + 6
(d) + 2.5

36. The final product of the reaction is

Cyclohexanone

$\xrightarrow[\text{(ii) H}^+/\text{H}_2\text{O}/\Delta]{\text{(i) dil. NaOH}}$

(a) [structure] (b) [structure]

(c) [structure with CH₂OH] (d) [structure with COOH]

(c) [cyclohexene]—CH_2OH (d) [cyclohexane]—$COOH$

37. Which is not true about the coordination compound $[Co(en)_2Cl_2]Cl$?
(a) It exhibits geometrical isomerism.
(b) It exhibits optical isomerism.
(c) It exhibits ionization isomerism.
(d) It is an octahedral complex.

38. Potassium permanganate acts as an oxidant in alkaline and acidic media. The final products formed from $KMnO_4$ in the two conditions are respectively
(a) MnO_4^{2-} and Mn^{3+} (b) Mn^{3+} and Mn^{2+}
(c) Mn^{2+} and Mn^{3+} (d) MnO_2 and Mn^{2+}

39. Using molecular orbital theory, compare the O_2^+ and O_2^- species and choose the incorrect option.
(a) O_2^+ have higher bond order than O_2^-.
(b) O_2^+ is more stable.
(c) O_2^+ is diamagnetic while O_2^- is paramagnetic.
(d) Both O_2^+ and O_2^- are paramagnetic.

40. Which of the following ores are concentrated by froth-floatation method?
(a) Cuprite (b) Sphalerite
(c) Siderite (d) Haematite

41. The formation of cyanohydrin from a ketone is an example of
(a) electrophilic addition
(b) nucleophilc addition
(c) nucleophilic substitution
(d) electrophilic substitution.

42. When sodium formate is heated with soda lime, it forms
(a) H_2 (b) CO
(c) CO_2 (d) water vapour.

43. 0.30 g of an organic compound containing C, H and O on combustion yields 0.44 g CO_2 and 0.18 g H_2O. If one mole of compound weighs 60, then molecular formula of the compound is
(a) $C_2H_4O_2$ (b) CH_2O
(c) C_3H_8O (d) C_4H_{12}

44. A primary alkyl halide would prefer to undergo
(a) S_N1 reaction (b) S_N2 reaction
(c) α-elimination (d) racemisation.

45. A reaction, $A + B \longrightarrow C + D + q$ is found to have a positive entropy change. The reaction will be
(a) possible at high temperature
(b) possible only at low temperature
(c) not possible at any temperature
(d) possible at any temperature.

46. If solubility of $Mg(OH)_2$ in water is 1.3×10^{-4} mol L^{-1}, then solubility (in mol L^{-1}) in 0.2 M KOH would be
(a) 2.19×10^{-4} (b) 2.19×10^{-6}
(c) 2.19×10^{-8} (d) 2.19×10^{-10}

47. If the standard electrode potential of Cu^{2+}/Cu electrode is 0.34 V, what is the electrode potential of 0.01 M concentration of Cu^{2+}?
Given : T = 298 K
(a) 0.399 V (b) 0.281 V
(c) 0.222 V (d) 0.176 V

48. For $A + B \longrightarrow C + D$; ΔH = 20 kJ mol^{-1}; the activation energy of the forward reaction is 85 kJ mol^{-1}. The activation energy of the reverse reaction is
(a) 100 kJ mol^{-1} (b) 65 kJ mol^{-1}
(c) 20 kJ mol^{-1} (d) 85 kJ mol^{-1}

49. 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. The percentage of chlorine present in the compound is
(a) 43.24% (b) 56.43%
(c) 98.25% (d) 37.56%

50. The probability density plots of 1s and 2s atomic orbitals are given in the figures:
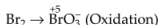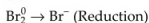

1s   2s
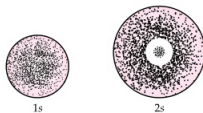
The density of dots in a region represents the probability density of finding electrons in that region.
On the basis of above diagrams, which one of the following statements is incorrect?
(a) 1s and 2s orbitals are spherical in shape.
(b) The probability of finding the electrons is maximum near the nucleus.
(c) The probability of finding the electrons at a given distance is equal in all directions.
(d) The probability density of electrons for 2s orbital decreases uniformly as distance from the nucleus increases.
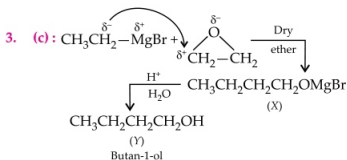
SOLUTIONS

1. (d): Bromine is both oxidized and reduced.

$$Br_2^0 \rightarrow Br^- \text{ (Reduction)}$$
$$Br_2 \rightarrow \overset{+5}{Br}O_3^- \text{ (Oxidation)}$$

2. (a): $\bar{\upsilon}_{max} = \dfrac{1}{\lambda_{min}} = R_H Z^2 \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2} \right]$

For λ_{min}, $n_1 = 1$, $n_2 = \infty$, $\Rightarrow \dfrac{1}{x} = R_H$
(For H-atom, $Z = 1$)

$\bar{\upsilon}_{min} = \dfrac{1}{\lambda_{max}} = R_H Z^2 \left[\dfrac{1}{2^2} - \dfrac{1}{3^2} \right] = \dfrac{1 \times 4}{x} \left[\dfrac{5}{36} \right]$
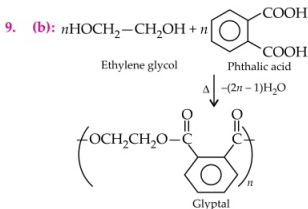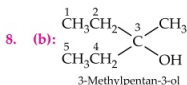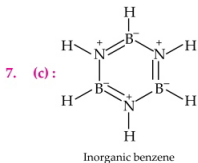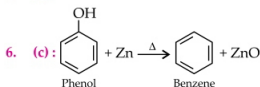(For He$^+$, $Z = 2$)

$\lambda_{max} = \dfrac{9x}{5}$

3. (c): $CH_3\overset{\delta-}{CH_2} - \overset{\delta+}{MgBr} + \overset{\delta-}{\underset{\delta+ CH_2-CH_2}{O}}$ $\xrightarrow{\text{Dry ether}}$

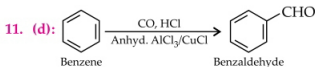$\xrightarrow[H_2O]{H^+}$ $CH_3CH_2CH_2CH_2OMgBr$ (X)

$CH_3CH_2CH_2CH_2OH$
(Y)
Butan-1-ol

4. (c): Rate $= -\dfrac{1}{5}\dfrac{\Delta[Br^-]}{\Delta t} = -\dfrac{\Delta[BrO_3^-]}{\Delta t} = -\dfrac{1}{6}\dfrac{\Delta[H^+]}{\Delta t}$

$\therefore \dfrac{\Delta[Br^-]}{\Delta t} = \dfrac{5}{6}\dfrac{\Delta[H^+]}{\Delta t}$

5. (c)

6. (c):
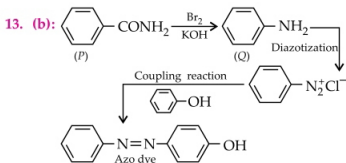Phenol $+ Zn \xrightarrow{\Delta}$ Benzene $+ ZnO$

7. (c):
Inorganic benzene

8. (b):
$\overset{1}{C}H_3\overset{2}{C}H_2 - \underset{\underset{OH}{|}}{\overset{3}{C}} - CH_3$
$\overset{5}{C}H_3\overset{4}{C}H_2$
3-Methylpentan-3-ol

9. (b): $nHOCH_2-CH_2OH + n$ [Phthalic acid COOH COOH]

Ethylene glycol   Phthalic acid

$\xrightarrow[-(2n-1)H_2O]{\Delta}$

Glyptal

10. (a): Maltose is made up of α-D-glucose.

11. (d): Benzene $\xrightarrow[\text{Anhyd. AlCl}_3/\text{CuCl}]{CO, HCl}$ CHO Benzaldehyde

12. (c)

13. (b): [CONH$_2$] $\xrightarrow[KOH]{Br_2}$ [NH$_2$] $\xrightarrow{\text{Diazotization}}$
(P) (Q)

$\xrightarrow{\text{Coupling reaction}}$ N$_2^+$Cl$^-$

N=N—OH
Azo dye

14. (d): $\lambda_{m(BaSO_4)}^\infty = \lambda_{Ba^{2+}}^\infty + \lambda_{SO_4^{2-}}^\infty$

$= \lambda_{m(BaCl_2)}^\infty + \lambda_{(H_2SO_4)}^\infty - 2\lambda_{(HCl)}^\infty$

$= x_1 + x_2 - 2x_3$

$\lambda_c^\infty = \dfrac{1}{2}\lambda_m^\infty(BaSO_4) = \dfrac{1}{2}(x_1 + x_2 - 2x_3)$

15. (d): $R \longrightarrow P$

$t_{1/2} = \dfrac{\ln 2}{k} = \dfrac{2.303 \times \log 2}{k} = \dfrac{0.693}{k}$

16. (d): According to Freundlich equation,

$\dfrac{x}{m} = kp^{1/n} \ (n > 1)$

Taking logarithm on both the sides,
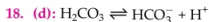
$\log \dfrac{x}{m} = \log k + \dfrac{1}{n}\log p$

Thus, ploting $\log \dfrac{x}{m}$ vs $\log p$ gives straight line

with slope $= \dfrac{1}{n}$ and intercept $= \log k$.

17. (a) : $\dfrac{V_X}{V_Y} = \sqrt{\dfrac{M_Y}{M_X}}$

$\dfrac{35}{29} = \sqrt{\dfrac{71}{M_X}}$

$M_X = 71 \times \left(\dfrac{29}{35}\right)^2 = 48.7$

18. (d) : $H_2CO_3 \rightleftharpoons HCO_3^- + H^+$

$K_1 = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]} \Rightarrow \dfrac{[HCO_3^-]}{[H_2CO_3]} = \dfrac{K_1}{[H^+]}$

We know pH = $- \log [H^+]$ = 7.4

$\log[H^+] = -7.4$, $[H^+] = 3.981 \times 10^{-8}$

$\therefore \dfrac{[HCO_3^-]}{[H_2CO_3]} = \dfrac{4.5 \times 10^{-7}}{3.981 \times 10^{-8}} = 11.3$

19. (b) :

Pyramidal

20. (d) : An electron withdrawing group increases the acidic strength of phenol while an electron donating group decreases the acidic strength of phenol. The electron withdrawing effect of $-NO_2$ group is greater than $-Cl$ group as it has positive charge on N atom.

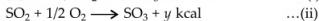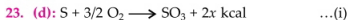Hence, (II) < (III) < (IV) < (I) is the correct increasing order of acidic strength.

21. (c) : Ozone hole is reduction in thickness of ozone layer in stratosphere.

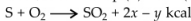**22. (c) :** $(x_A)_{vapour} = \dfrac{p_A}{p_{Total}} = \dfrac{(x_A)_{liquid}\, p_A^o}{p_{Total}}$

$\Rightarrow \dfrac{(x_A)_{vapour}}{(x_A)_{liquid}} = \dfrac{p_A^o}{p_{Total}}$
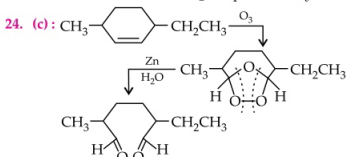
As B is less volatile, then $p_{Total} < p_A^o$

$\therefore \dfrac{(x_A)_{vapour}}{(x_A)_{liquid}} > 1$ or $(x_A)_{vapour} > (x_A)_{liquid}$

23. (d) : $S + 3/2\ O_2 \longrightarrow SO_3 + 2x$ kcal   ...(i)

$SO_2 + 1/2\ O_2 \longrightarrow SO_3 + y$ kcal   ...(ii)

Now, subtract eq. (ii) from (i), we get

$S + O_2 \longrightarrow SO_2 + 2x - y$ kcal

$\therefore$ Heat of formation of SO_2 is equal to $2x - y$ kcal.

24. (c) :

25. (a) :

Cyclohexene   3-Bromocyclohex-1-ene
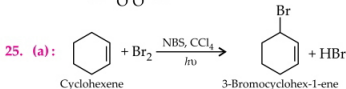
26. (c)   **27. (b)**

28. (c) : This is mainly due to the reason that as the size of the cation increases down the group, the heat of hydration decreases while the lattice energy remains the same because the sulphate ion is so big that increase in size of the cations down the group does not make any difference. Solubility decreases in following order

$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

29. (b) : In reaction (b), O_2 is evolved, therefore, it represents the reducing action of H_2O_2. I_2 changes to $2I^-$.

30. (d)

31. (d) : For the reaction : $PbO_2 \rightarrow PbO$

given that $\Delta G < 0$ thus the reaction will be spontaneous in forward direction.

For the reaction : $SnO_2 \rightarrow SnO$

given that $\Delta G > 0$ thus reaction is non-spontaneous in forward direction but spontaneous in reverse direction. This shows Pb^{2+} for lead and Sn^{4+} for tin are most probable oxidation states.

32. (a) : Number of oxide ions (O^{2-}) per unit cell

$= 8 \times \dfrac{1}{8} + 6 \times \dfrac{1}{2} = 4$ (ccp arrangement)

Number of A atom per unit cell $= \dfrac{1}{8} \times (2 \times 4)$

[$\because$ Tetrahedral voids = 2 × Number of spheres]

Number of B atom per unit cell $= \dfrac{1}{2} \times 4$

[$\because$ Number of octahedral voids = Number of spheres]
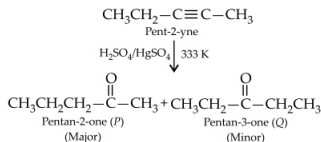
Hence the formula of the solid = AB_2O_4

33. (c) : No. of moles of $A = \dfrac{x}{40}$
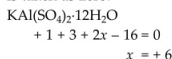
No. of atoms of $A = \dfrac{x}{40} \times N_A = y$

No. of moles of $B = \dfrac{2x}{80} = \dfrac{x}{40}$

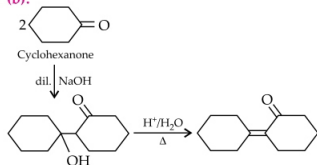Now, no. of atoms of $B = \dfrac{x}{40} N_A = y$

34. (a) : In case of unsymmetrical alkyne, which is non-terminal, mixture of two isomeric ketones is obtained in which methyl ketone predominates.

$$CH_3CH_2-C\equiv C-CH_3$$
Pent-2-yne

$$\xrightarrow[333\ K]{H_2SO_4/HgSO_4}$$

$$\underset{\substack{\text{Pentan-2-one }(P)\\(\text{Major})}}{CH_3CH_2CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} + \underset{\substack{\text{Pentan-3-one }(Q)\\(\text{Minor})}}{CH_3CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2CH_3}$$

35. (c) : Since water is a neutral molecule, the sum of the oxidation numbers of all the atoms in water is taken as zero.

$KAl(SO_4)_2 \cdot 12H_2O$

$+ 1 + 3 + 2x - 16 = 0$

$x = +6$

36. (b) :

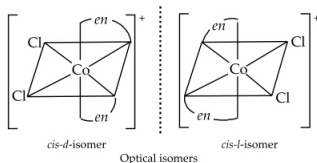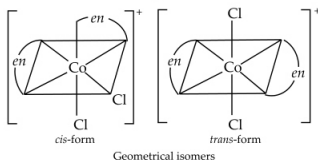Cyclohexanone

dil. NaOH ↓

$\xrightarrow[\Delta]{H^+/H_2O}$

37. (c) : Ionization isomerism arises when the coordination compounds give different ions in solution, this condition is not satisfied with $[Co(en)_2Cl_2]Cl$.
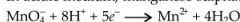
It is an octahedral complex.

cis-form   trans-form
Geometrical isomers

cis-d-isomer   cis-l-isomer
Optical isomers

38. (d) : In alkaline medium, $KMnO_4$ is first reduced to manganate ion and then to insoluble manganese dioxide.

$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$
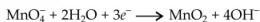
In acidic medium, manganese sulphate is formed.

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

39. (c) : For O_2^+,

$\sigma 1s^2,\ \sigma^*1s^2,\ \sigma 2s^2,\ \sigma^*2s^2,\ \sigma 2p_z^2,\ (\pi 2p_x^2 = \pi 2p_y^2),\ \pi^*2p_x^1$

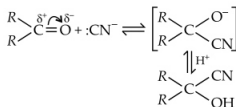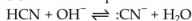Bond order $= \dfrac{1}{2}(N_b - N_a)$

$= \dfrac{1}{2}(10 - 5) = 2.5$

For O_2^-,

$\sigma 1s^2,\ \sigma^*1s^2,\ \sigma 2s^2,\ \sigma^*2s^2,\ \sigma 2p_z^2,\ (\pi 2p_x^2 = \pi 2p_y^2),\ (\pi^*2p_x^2 = \pi^*2p_y^1)$

Bond order $= \dfrac{1}{2}(N_b - N_a)$

$= \dfrac{1}{2}(10 - 7) = 1.5$

40. (b) : Froth-floatation method is used for concentration of sulphide ores.

41. (b) : It is nucleophilic additon reaction.

$HCN + OH^- \rightleftharpoons :CN^- + H_2O$

42. (a) : $HCOONa + NaOH \xrightarrow[\text{Heat}]{CaO} H_2 + Na_2CO_3$
Sod. formate   Hydrogen

43. (a) : Weight of carbon $= 12 \times$ Moles of CO_2

$= \dfrac{12 \times 0.44}{44} = 0.12$ g

Weight of hydrogen $= 2 \times$ Moles of H_2O

$= \dfrac{2 \times 0.18}{18} = 0.02$ g

Weight of oxygen $= 0.30 - (0.12 + 0.02) = 0.16$ g

Element	C	H	O
Weight ratio	0.12	0.02	0.16
Mole ratio	0.01	0.02	0.01

Simple ratio = 1 : 2 : 1
Empirical formula = CH_2O
Molecular weight = (Empirical weight)$_n$
$\Rightarrow$ $60 = 30 \times n$ $\Rightarrow$ $n = 2$
$\therefore$ Molecular formula = $(CH_2O)_2 = C_2H_4O_2$

44. (b)

45. (d): Here, ΔH = –ve and ΔS = +ve.
$\Delta G = \Delta H - T\Delta S$
For the reaction to be spontaneous, ΔG should be –ve which will be so at any temperature.

46. (d): For $Mg(OH)_2$
$K_{sp} = 4S^3 = 4 \times (1.3 \times 10^{-4})^3 = 8.788 \times 10^{-12}$
Let the solubility of $Mg(OH)_2$ in 0.2 M KOH solution = S_0
Then $Mg^{2+} = S_0$ mol L^{-1},
$OH^- = (2S_0 + 0.2)$ mol L^{-1}
$K_{sp} = 8.788 \times 10^{-12} = S_0 (2S_0 + 0.2)^2$
Here, $2S_0 + 0.2 = 0.2$ [$\because 2S_0 <<< 0.2$]
$\therefore$ $8.788 \times 10^{-12} = 0.04\, S_0$
$$S_0 = \frac{8.788 \times 10^{-12}}{0.04} = 2.19 \times 10^{-10}\, mol\, L^{-1}$$

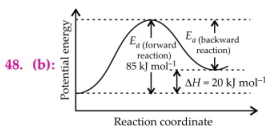**47. (b):** The cell reaction is $Cu^{2+} + 2e^- \rightarrow Cu$
$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[Cu^{2+}]}$$
or, $E_{cell} = E_{cell}^{\circ} + \frac{0.0591}{2} \log [Cu^{2+}]$

$= 0.34 + \frac{0.0591}{2} \log 0.01 = 0.34 - 0.0591$

$= 0.2809 \approx 0.281$ V

48. (b):

Given: $\Delta H = 20$ kJ mol^{-1}
Since $\Delta H = E_{a(forward\ reaction)} - E_{a(backward\ reaction)}$
Given: $E_{a(forward)} = 85$ kJ mol^{-1}
$\therefore$ $E_{a(backward)} = E_{a(forward)} - \Delta H$
$= 85 - 20$
$= 65$ kJ mol^{-1}

49. (d): The mass of the substance taken = 0.3780 g
Mass of AgCl formed = 0.5740 g
Now, 1 mole of AgCl = 1 g atom of Cl
or (108 + 35.5) = 143.5 g of AgCl = 35.5 g of Cl
Applying the relation,
Percentage of chlorine
$$= \frac{35.5}{143.5} \times \frac{Mass\ of\ AgCl\ formed}{Mass\ of\ substance\ taken} \times 100$$
$$= \frac{35.5}{143.5} \times \frac{0.5740}{0.3780} \times 100 = 37.56\%$$

50. (d): The probability density of electrons for 2s orbital first increases then decreases and after that it begins to increase again.

■■

SAMPLE PAPER

CBSE CLASS XII

BOARD EXAMINATION 2014

Time : 3 hrs.   Marks : 70

GENERAL INSTRUCTIONS

(i)   All questions are compulsory.

(ii) Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.

(iii) Question numbers 9 to 18 are short-answer questions and carry 2 marks each.

(iv) Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.
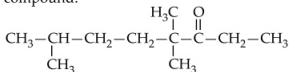
(v)   Question numbers 28 to 30 are long-answer questions and carry 5 marks each.

(vi) Use Log Tables, if necessary. Use of calculator is not allowed.

1. Why is hydrogen sulphide, with greater molar mass, a gas, while water a liquid at room temperature?

2. Give the IUPAC name of the following compound:

$$CH_3-CH-CH_2-CH_2-\overset{\overset{H_3C}{|}\,\,\overset{O}{\parallel}}{C}-\overset{|}{C}-CH_2-CH_3$$
$$\qquad\quad |\qquad\qquad\qquad\;\; |$$
$$\qquad CH_3\qquad\qquad\quad CH_3$$

3. For the reaction $A \longrightarrow B$, rate becomes eight times when the concentration of A is doubled. What is the order of the reaction?

4. What is the cause of Brownian movement observed in colloidal solution?

5. Write the reaction that indicates the presence of a primary alcoholic group in glucose.

6. Draw the structure of xenon oxyfluoride molecule which is isoelectronic with IF_5.

7. What is the shape of the complex used as an antitumour agent in treatment of cancer?

8. Dipole moment of phenol is smaller than that of methanol. Why?

9. (a) Write nernst equation to calculate the cell potential of the given cell:

   $$Mg_{(s)} \mid Mg^{2+}_{(aq)} \mid\mid Ag^{+}_{(aq)} \mid Ag_{(s)}$$

   (b) Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

10. Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ($t_{1/2}$) of the reaction.

OR

Show that in a first order reaction, time required for 99% completion is twice the time required for the completion of 90% reaction.

11. Do the following conversions:

   (i) Bromomethane to propanone

   (ii) 1-Bromopropane to 2-bromopropane

12. How will you distinguish between the following pairs of compounds:

   (i) Chloroform and carbon tetrachloride

   (ii) Benzyl chloride and chlorobenzene?

13. For a chemical reaction, a graph is shown below:
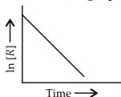
   (i) What is the order of the reaction?

   (ii) What is the unit of rate constant k for the reaction?

14. Explain why $[Fe(H_2O)_6]^{3+}$ has magnetic moment value of 5.92 BM whereas $[Fe(CN)_6]^{3-}$ has a value of only 1.74 BM.

15. Give reason for the following:
    (i) Aniline is a weaker base than cyclohexylamine.
    (ii) Ammonolysis of alkyl halide does not give a corresponding amine in pure state.

16. Write the following reactions:
    (i) Carbylamine reaction
    (ii) Coupling reaction

17. Sodium has a *bcc* structure with nearest neighbour distance 365.9 pm. Calculate its density. (Atomic mass of sodium = 23)

18. If NaCl is doped with 10^{-3} mol % of $SrCl_2$, what is the concentration of cation vacancies?

19. In the button cell widely used in watches, the following reaction takes place:
    $Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$
    Determine $E°$ and $\Delta G°$ for the reaction.
    Given: $E°_{Ag^+/Ag} = 0.80$ V, $E°_{Zn^{2+}/Zn} = -0.76$ V

20. Explain what is observed:
    (i) when a beam of light is passed through a colloidal solution.
    (ii) an electrolyte is added to hydrated ferric oxide sol.
    (iii) electric current is passed through a colloidal solution.

21. (a) Name the element that is purified by
       (i) zone refining process
       (ii) van Arkel method.
    (b) The value of $\Delta_f G°$ for formation of Cr_2O_3 is -540 kJ mol^{-1} and that of Al_2O_3 is -827 kJ mol^{-1}. Is the reduction of Cr_2O_3 possible with aluminium?

    OR

    (a) What is the role of depressant in froth floatation process? Give one example.
    (b) Describe the principle involved in Mond process for refining of nickel.

22. Write balanced chemical equations for the following reactions:
    (i) $Ca_3P_2 + H_2O \longrightarrow$
    (ii) $F_2 + H_2O \underset{\text{(hot)}}{\longrightarrow}$
    (iii) $XeF_4 + H_2O \longrightarrow$

23. (a) Draw the structures of the following molecules:
       (i) $H_2S_2O_8$ (ii) IF_7
    (b) Unlike phosphorus, nitrogen shows little tendency for catenation. Why?
    (c) What happens when orthophosphorous acid is heated?

24. (a) Of the two bases named below, which one is present in RNA and which one is present in DNA?
       (i) Thymine   (ii) Uracil
    (b) The deficiency of which vitamin causes the following diseases?
       (i) Pernicious anaemia
       (ii) Xerophthalmia
    (c) Give one structural difference between amylose and amylopectin.

25. Gaurav took his father to doctor for routine check-up. He told his doctor about the symptoms like increase in appetite, excessive thirst, frequent urination, feeling fatigued, high depression. After examine, doctor advised him to add artifical sweeteners in tea or coffee.
    (i) From which disease, Gaurav's father was suffering? What values are shown by Gaurav?
    (ii) Name two artificial sweeteners that Gaurav's father must use instead of using sugar.

26. (a) Write the reaction of preparation of melamine-formaldehyde resin.
    (b) How is dacron obtained from ethylene glycol and terephthalic acid?
    (c) Write the formulae of the monomers of
       (i) Natural rubber (ii) Nylon 6.

27. Write the mechanism for the preparation of ethene from ethanol.

28. (a) State Raoult's law for solutions of volatile liquids. Explain the meaning of positive and negative deviations from Raoult's law. Also give examples.
    (b) Vapour pressure of chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg respectively. Calculate the vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of CH_2Cl_2 at 298 K.

OR

(a) Define the term osmotic pressure. Describe how the molecular mass of a substance can be determined by a method based on measurement of osmotic pressure.

(b) At 300 K, 36 g of glucose $C_6H_{12}O_6$ present per litre in its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of another solution is 1.52 bar at the same temperature, calculate the concentration of the other solution.

29. (a) Answer the following questions with reasons.
   (i) Which element of the first transition series has highest second ionisation enthalpy?
   (ii) Which element of the first transition series has highest third ionisation enthalpy?
   (iii) Which element of the first transition series has lowest enthalpy of atomisation?

(b) Complete the following reactions:
   (i) $SO_2 + Cr_2O_7^{2-} + H^+ \longrightarrow$
   (ii) $S_2O_3^{2-} + MnO_4^- + H_2O \longrightarrow$

OR

(a) When a chromite ore (A) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (B) is obtained. After treatment of this yellow solution with sulphuric acid, compound (C) can be crystallised from the solution. When compound (C) is treated with KCl, orange crystals of compound (D) crystallise out. Identify A to D and also write the reactions involved.

(b) Write the structures of
   (i) dichromate ion
   (ii) manganate ion.

30. (a) (i) Carboxylic acid is a stronger acid than phenol. Why?
   (ii) Arrange the following compounds in decreasing order of their acidic strength: C_6H_5COOH, CH_3COOH, $HCOOH$

(b) An organic compound (A) having molecular formula $(C_8H_{16}O_2)$ was hydrolysed with dilute sulphuric acid to give two compounds (B) and (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

OR

(a) How will you prepare the following compounds starting with benzene:
   (i) Benzaldehyde (ii) Acetophenone?

(b) Write the following conversions in not more than two steps:
   (i) Benzaldehyde to α-hydroxyphenylacetic acid
   (ii) Bromobenzene to 1-phenylethanol
   (iii) Benzaldehyde to benzophenone

SOLUTIONS

1. Water molecules are associated with intermolecular H-bonding because oxygen is smaller in size and more electronegative than sulphur.
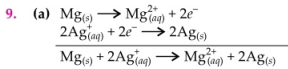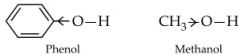
2.

4, 4, 7-Trimethyloctan-3-one
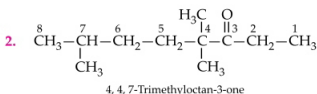
3. It is a third order reaction.
Rate = $k[A]^3$
If $[A]$ is doubled, rate will become eight times.
Rate = $k[2A]^3 = 8k[A]^3$

4. Brownian movement is explained due to the unbalanced bombardment of the particles by the molecules of the dispersion medium.

5.

6. $XeOF_4$ is isoelectronic with IF_5 and has square pyramidal structure.

7. cis-Platin $[Pt(NH_3)_2Cl_2]$, is used as an antitumour agent in treatment of cancer. The shape of complex is square planar.

cis-Platin

8. In phenol, C—O bond is less polar due to electron withdrawing effect of the benzene ring whereas in methanol, C—O bond is more polar due to electron releasing effect of the methyl group.

Phenol   Methanol

9. (a) $Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2e^-$

$2Ag^+_{(aq)} + 2e^- \longrightarrow 2Ag_{(s)}$

$\overline{Mg_{(s)} + 2Ag^+_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + 2Ag_{(s)}}$

$E_{cell} = E^\circ_{cell} - \dfrac{2.303\,RT}{nF} \log \dfrac{[Mg^{2+}]}{[Ag^+]^2}$

(b) pH = 10

pH = $-\log[H^+]$

$\Rightarrow$ $[H^+] = 10^{-10}$ mol L^{-1}

$E_{H^+/H_2} = E^\circ_{H^+/H_2} - \dfrac{0.0591}{1} \log \dfrac{1}{[H^+]}$

$= 0 - \dfrac{0.0591}{1} \log \dfrac{1}{10^{-10}} = -\dfrac{0.0591}{1} \log 10^{10}$

$E_{H^+/H_2} = -0.591$ V

10. For a first order reaction,

$t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]}$

$t_{99.9\%} = \dfrac{2.303}{k} \log \dfrac{[R]_0}{\left([R]_0 - \dfrac{99.9}{100}[R]_0\right)}$

$= \dfrac{2.303}{k} \log \dfrac{[R]_0}{0.001[R]_0}$

$= \dfrac{2.303}{k} \log 1000 = \dfrac{2.303}{k} \times \log 10^3 = \dfrac{6.909}{k}$

$t_{1/2} = \dfrac{0.693}{k}$

$\Rightarrow$ $\dfrac{t_{99.9\%}}{t_{1/2}} = \dfrac{6.909}{k} \times \dfrac{k}{0.693} \simeq 10$

OR

For a first order reaction,

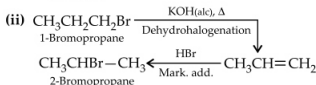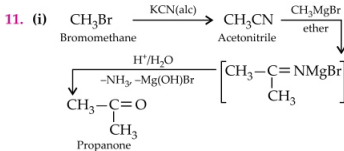$t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]}$

$t_{99\%} = \dfrac{2.303}{k} \log \dfrac{[R]_0}{\left([R]_0 - \dfrac{99}{100}[R]_0\right)}$

$= \dfrac{2.303}{k} \log 100 = \dfrac{2.303 \times 2}{k} = \dfrac{4.606}{k}$

$t_{90\%} = \dfrac{2.303}{k} \log \dfrac{[R]_0}{\left([R]_0 - \dfrac{90[R]_0}{100}\right)}$

$= \dfrac{2.303}{k} \log 10 = \dfrac{2.303}{k} \times 1$

$\dfrac{t_{99\%}}{t_{90\%}} = \dfrac{4.606}{k} \times \dfrac{k}{2.303} = 2 \Rightarrow t_{99\%} = 2t_{90\%}$

11. (i) CH_3Br $\xrightarrow{KCN(alc)}$ CH_3CN $\xrightarrow{CH_3MgBr}{ether}$

Bromomethane   Acetonitrile

$\xrightarrow[-NH_3, -Mg(OH)Br]{H^+/H_2O}$ $\left[CH_3 - C = NMgBr \atop \qquad\quad | \atop \qquad\quad CH_3\right]$

$CH_3 - C = O$
$\qquad\quad |$
$\qquad\quad CH_3$

Propanone

(ii) $CH_3CH_2CH_2Br$ $\xrightarrow[\text{Dehydrohalogenation}]{KOH(alc), \Delta}$

1-Bromopropane

$CH_3CHBr - CH_3$ $\xleftarrow[\text{Mark. add.}]{HBr}$ $CH_3CH = CH_2$

2-Bromopropane

12. (i) On heating chloroform and carbon tetrachloride with aniline and ethanolic potassium hydroxide separately, chloroform forms foul smelling isocyanide but carbon tetrachloride does not form this compound.

(ii) On adding sodium hydroxide and silver nitrate to both the compounds, benzyl chloride forms white precipitate of AgCl but chlorobenzene does not form white precipitate.

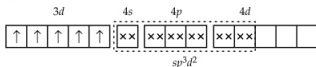13. (i) For a first order reaction
$\ln[R] = -kt + \ln[R]_0$
Hence, the graph shows it is a first order reaction.

(ii) Unit of rate constant k, for a first order reaction is s^{-1}.
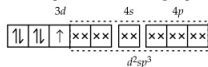
14. Fe (26) : $[Ar]\, 3d^6\, 4s^2$
$Fe^{3+} : [Ar]\, 3d^5$
In $[Fe(H_2O)_6]^{3+}$, since H_2O is a weak field ligand, all the $3d^5$ electrons remain unpaired. Six lone pairs of H_2O molecules are coordinated to six sp^3d^2 hybrid orbitals.

Magnetic moment of five unpaired electrons
$= \sqrt{n(n+2)}$ BM $= \sqrt{35} = 5.92$ BM

In $[Fe(CN)_6]^{3-}$, since CN^- is a strong field ligand and unpaired electrons get paired.


Unpaired electrons = 1

Manetic moment $= \sqrt{n(n+2)} = \sqrt{3} = 1.74$ BM

15. (i) In case of aniline, the lone pair of electrons on the nitrogen atom is delocalized over the benzene ring. As a result, the electron density on nitrogen atom decreases as there is positive charge on nitrogen in three out of five resonating structures.
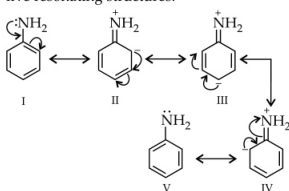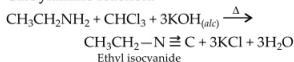

Whereas in cyclohexylamine, no such delocalization is possible.

(ii) Ammonolysis of alkyl halide first gives primary amine. Thus primary amine obtained behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines, and finally quaternary ammonium salt.
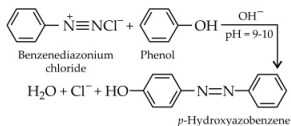
$$RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4\overset{+}{N}\overset{-}{X}$$
$$\quad 1° \qquad\quad 2° \qquad\quad 3° \qquad \text{Quaternary}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{ammonium}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{salt}$$
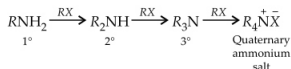
This mixture is difficult to separate.

16. (i) **Carbylamine reaction:**

$$CH_3CH_2NH_2 + CHCl_3 + 3KOH_{(alc)} \xrightarrow{\Delta}$$
$$CH_3CH_2-N \cong C + 3KCl + 3H_2O$$
$$\qquad\text{Ethyl isocyanide}$$

(ii) **Coupling reaction:**

$$H_2O + Cl^- + HO-\!\!\!\!\bigcirc\!\!\!\!-N=N-\!\!\!\!\bigcirc$$

p-Hydroxyazobenzene

17. For the *bcc* structure, nearest neighbour distance (d) is related to the edge (a) as $d = \dfrac{\sqrt{3}}{2}a$

or $a = \dfrac{2}{\sqrt{3}}d = \dfrac{2}{1.732} \times 365.9 = 422.5$ pm

For *bcc* structure, $Z = 2$

For sodium, $M = 23$

$\therefore \quad \rho = \dfrac{Z \times M}{a^3 \times N_A}$

$= \dfrac{2 \times 23 \text{ g mol}^{-1}}{(422.5 \times 10^{-10} \text{ cm})^3 \times (6.02 \times 10^{23} \text{ mol}^{-1})}$

$= 1.013$ g/cm^3

18. The number of cation vacancies created in the lattice of NaCl is equal to the number of divalent Sr^{2+} ions added as one Sr^{2+} will replace two Na^+.

Conc. of $Sr^{2+} = 10^{-3}$ mol % $= \dfrac{10^{-3}}{100} = 10^{-5}$ mol

1 mole of $Sr^{2+} = 6.023 \times 10^{23}$ Sr^{2+} ions
10^{-5} mole of $Sr^{2+} = 6.023 \times 10^{23} \times 10^{-5}$
$\qquad\qquad\qquad = 6.023 \times 10^{18}$ Sr^{2+} ions

Hence, the concentration of cation vacancies is 6.023×10^{18}.

19. At anode : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$
$E°_{Zn/Zn^{2+}} = -E°_{Zn^{2+}/Zn}$
$\qquad\qquad = -(- 0.76) = +0.76$ V

At cathode :
$Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \longrightarrow 2Ag_{(s)} + 2OH^-_{(aq)},$
$\qquad\qquad\qquad\qquad\qquad\qquad E°_{Ag^+/Ag} = 0.80$ V
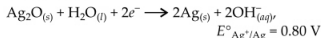
$E°_{cell}$ = Standard oxidation potential of zinc electrode + Standard reduction potential of silver electrode

Thus,
$E°_{cell} = E°_{Zn/Zn^{2+}} + E°_{Ag^+/Ag}$
$\qquad = 0.76 + 0.80 = 1.56$ V

$\Delta G°_{cell} = -nFE°_{cell}$
$\qquad = -2 \times 96500 \times 1.56$
$\qquad = -301080$ J mol^{-1}
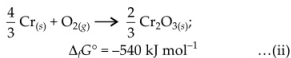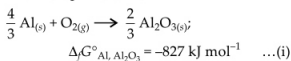$\qquad = -301.08$ kJ mol^{-1}

20. (i) Scattering of light by the colloidal particles takes place and the path of light becomes visible (Tyndall effect).

(ii) The positively charged colloidal particles of $Fe(OH)_3$ get coagulated by the oppositely charged Cl^- ions provided by NaCl.
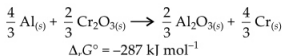
(iii) On passing an electric current, colloidal particles move towards the oppositely charged electrode where they lose their charge and get coagulated.

21. (a) (i) Germanium   (ii) Zirconium

(b) The two equations are:

$$\frac{4}{3}Al_{(s)} + O_{2(g)} \longrightarrow \frac{2}{3}Al_2O_{3(s)};$$
$$\Delta_f G^\circ_{Al, Al_2O_3} = -827 \text{ kJ mol}^{-1} \quad …(i)$$

$$\frac{4}{3}Cr_{(s)} + O_{2(g)} \longrightarrow \frac{2}{3}Cr_2O_{3(s)};$$
$$\Delta_r G^\circ = -540 \text{ kJ mol}^{-1} \quad …(ii)$$

Subtracting Eq. (ii) from Eq. (i), we have,

$$\frac{4}{3}Al_{(s)} + \frac{2}{3}Cr_2O_{3(s)} \longrightarrow \frac{2}{3}Al_2O_{3(s)} + \frac{4}{3}Cr_{(s)}$$
$$\Delta_r G^\circ = -287 \text{ kJ mol}^{-1}$$

As $\Delta_r G^\circ$ of the reaction is –ve, reduction of Cr_2O_3 is possible with aluminium.

OR

(a) In froth floatation process, the role of the depressant is to prevent one type of sulphide ore particles from forming the froth with air bubbles. For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from forming the froth as it forms a complex with zinc but allows PbS to form froth.

(b) In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl:

$$Ni + 4CO \xrightarrow{330 - 350\ K} Ni(CO)_4$$
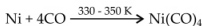
The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal:

$$Ni(CO)_4 \xrightarrow{450 - 470\ K} Ni + 4CO$$
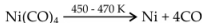
22. (i) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

(ii) $3F_2 + 3H_2O_{(hot)} \longrightarrow 6HF + O_3$

(iii) $6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 4Xe + 24HF + 3O_2$

23. (a) (i)   (ii)
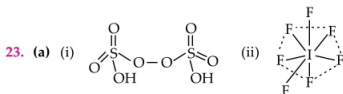
(b) Due to smaller size, the lone pairs of electrons on the two N-atoms repel the bond pair of N—N bond. While because of comparatively larger size of P, the lone pairs of electrons on the two P atoms do not repel the bond pair of the P—P bond to the same extent. As a result,

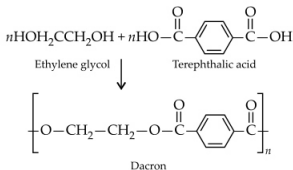N—N single bond is weaker than P—P single bond. Consequently, nitrogen shows little tendency for catenation.

(c) When H_3PO_3 is heated, it undergoes disproportionation to form PH_3 and H_3PO_4 with oxidation states of –3 and +5 respectively.

$$4\overset{+3}{H_3PO_3} \xrightarrow{Heat} \overset{-3}{PH_3} + \overset{+5}{H_3PO_4}$$

Orthophosphorous   Phosphine   Orthophosphoric
acid   acid
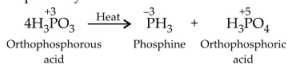
24. (a) (i) Thymine is present in DNA.
(ii) Uracil is present in RNA.

(b) (i) Pernicious anaemia—Vitamin B_{12}
(ii) Xerophthalmia—Vitamin A

(c) Amylose is a long unbranched chain of α-D-(+)-glucose units held by C1–C4 glycosidic linkage.
Amylopectin is a branched chain polymer of α-D-glucose units in which chain is formed by C1–C4 glycosidic linkage whereas branching occurs by C1–C6 glycosidic linkage.

25. (i) Diabetes, caring nature.
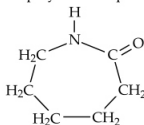(ii) Sucralose, saccharin.

26. (a)
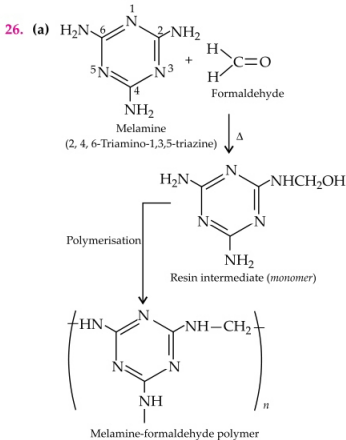
(b) Dacron is obtained by condensation polymerization of ethylene glycol and terephthalic acid.

$n\text{HOH}_2\text{CCH}_2\text{OH} + n\text{HO}-\overset{\text{O}}{\underset{}{\text{C}}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\underset{}{\text{C}}}-\text{OH}$

Ethylene glycol   Terephthalic acid

$$\left[-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\overset{\text{O}}{\underset{}{\text{C}}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\underset{}{\text{C}}}- \right]_n$$

Dacron

(c) (i) Natural rubber is a polymer of isoprene (2-methyl-1,3-butadiene).

$$\text{H}_2\text{C}=\overset{\underset{|}{\text{CH}_3}}{\text{C}}-\text{CH}=\text{CH}_2$$
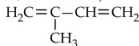
(ii) Nylon 6 is a polymer of caprolactam.

27. Mechanism

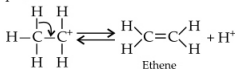Step 1 : Formation of protonated alcohol:
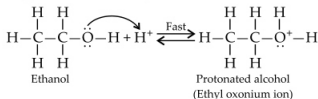
Step 2 : Formation of carbocation:

It is the slowest step and hence, the rate determining step of the reaction.
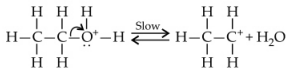
Step 3 : Formation of ethene by elimination of a proton.

The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

28. (a) Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.

Thus, for components 1 and 2

$$p_1 \propto x_1, \qquad p_2 \propto x_2$$

and $\quad p_1 = p_1^o x_1, \qquad p_2 = p_2^o x_2$

where p_1^o and p_2^o are the vapour pressures of pure components 1 and 2 at the same temperature.

If partial vapour pressures of the components are higher than the value calculated from Raoult's law, the solution exhibits positive deviation.

In this case, the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules and leads to increase in vapour pressure. *e.g.*, mixture of ethanol and acetone.

If partial vapour pressures of the components are lower than the value calculated from Raoult's law, the solution exhibits negative deviation.

In this case, the intermolecular attractive forces between solute-solute and solvent-solvent are weaker than those between solute-solvent and leads to decrease in vapour pressure. e.g., mixture of phenol and aniline.

(b) Molar mass of CH_2Cl_2
$$= 12 \times 1 + 1 \times 2 + 35.5 \times 2 = 85 \text{ g mol}^{-1}$$

Molar mass of $CHCl_3$
$$= 12 \times 1 + 1 \times 1 + 35.5 \times 3 = 119.5 \text{ g mol}^{-1}$$

Moles of $CH_2Cl_2 = \dfrac{40 \text{ g}}{85 \text{ g mol}^{-1}} = 0.47 \text{ mol}$

Moles of $CHCl_3 = \dfrac{25.5 \text{ g}}{119.5 \text{ g mol}^{-1}} = 0.213 \text{ mol}$

Total number of moles $= 0.47 + 0.213$
$$= 0.683 \text{ mol}$$

$$x_{CH_2Cl_2} = \frac{0.47}{0.683} = 0.688$$

$$p_{total} = p_1^o + (p_2^o - p_1^o) x_2$$
$$= 200 + (415 - 200) \times 0.688$$
$$= 200 + 147.9 = 347.9 \text{ mm Hg}$$

OR

(a) Osmotic pressure of the solution is the pressure that just stops the flow of solvent from its side to solution side across a semipermeable membrane.

$$\pi V = nRT$$
$$\pi V = \frac{W_B}{M_B} RT$$
$$\Rightarrow M_B = \frac{W_B \times R \times T}{\pi \times V}$$

(b) $\pi(\text{glucose}) = \dfrac{n}{V} RT$
$$= \frac{w_1}{M_1 V} RT$$

$$4.98 = \left(\frac{36}{180 \times 1}\right) RT = 0.2 \, RT \qquad \dots(i)$$

$$\pi(\text{unknown}) = \frac{w_2}{V \times M_2} RT = M'RT$$
$$[\because M' = \text{Molarity}]$$

$$1.52 = M' \, RT \qquad \dots(ii)$$

By dividing eqn. (ii) by (i),

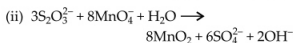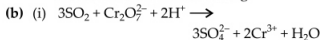$$\therefore \quad \frac{1.52}{4.98} = \frac{M' \, RT}{0.2 \, RT}$$

$$\therefore \quad M' = 0.2 \times \frac{1.52}{4.98} = 0.061 \text{ M}$$

29. (a) (i) Cu. This is because electronic configuration of Cu is $3d^{10} 4s^1$. After loss of one $4s$ electron, it acquires stable configuration of $3d^{10}$. Hence, removal of second electron is very difficult.
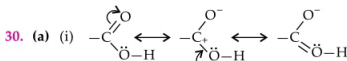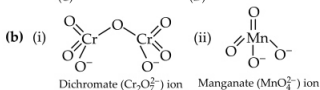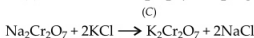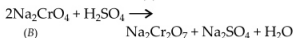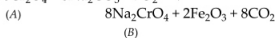
(ii) Zn. This is because electronic configuration of Zn is $3d^{10} 4s^2$ and that of Zn^{2+} is $3d^{10}$ which is again fully filled and hence very stable. Removal of third electron requires very high energy.

(iii) Zn. This is because it has completely filled $3d$ subshell and no unpaired electron is available for metallic bonding.
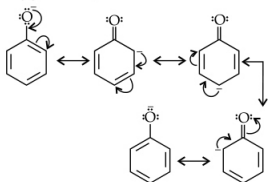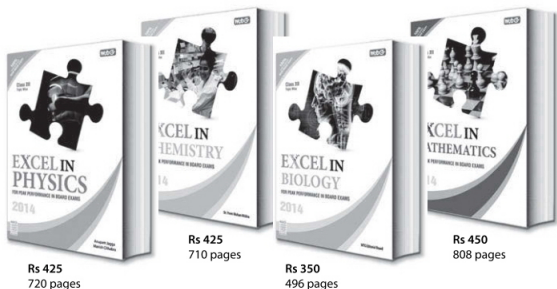
(b) (i) $3SO_2 + Cr_2O_7^{2-} + 2H^+ \longrightarrow$
$$3SO_4^{2-} + 2Cr^{3+} + H_2O$$

(ii) $3S_2O_3^{2-} + 8MnO_4^- + H_2O \longrightarrow$
$$8MnO_2 + 6SO_4^{2-} + 2OH^-$$

OR

(a) $A = FeCr_2O_4$, $B = Na_2CrO_4$,
$C = Na_2Cr_2O_7 \cdot 2H_2O$, $D = K_2Cr_2O_7$

$\underset{(A)}{4FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \longrightarrow$
$$\underset{(B)}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$$

$\underset{(B)}{2Na_2CrO_4} + H_2SO_4 \longrightarrow$
$$\underset{(C)}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

$\underset{(C)}{Na_2Cr_2O_7} + 2KCl \longrightarrow \underset{(D)}{K_2Cr_2O_7} + 2NaCl$

(b) (i)

Dichromate $(Cr_2O_7^{2-})$ ion

(ii)

Manganate (MnO_4^{2-}) ion

30. (a) (i)

The negative charge in these structures is delocalised over two more electronegative oxygen atoms, hence more stable.

The negative charge in these structures is at the less electronegative carbon atom, hence less stable.

(ii) $HCOOH > C_6H_5COOH > CH_3COOH$

$-CH_3$ group being electron releasing, decreases the acidity while as formic acid does not contain alkyl group, it is stronger acid. Phenyl group increases the acidity contrary to the decrease expected due to resonance effect.

(b) On hydrolysis with dilute sulphuric acid, (*A*) with $C_8H_{16}O_2$ molecular formula gives (*B*) and (*C*). (*A*) must be an ester. Since (*C*) on dehydration gives but-1-ene, so (*C*) must be an alcohol *i.e.*, butan-1-ol. Furthermore, oxidation of (*C*) with chromic acid produces (*B*), this means both acid (*B*) and alcohol (*C*) must have same number of carbon atoms.

$$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_2CH_2CH_3$$
(*A*) ($C_8H_{16}O_2$)
Butyl butanoate

dil. H_2SO_4 | Hydrolysis

$$CH_3CH_2CH_2COOH + CH_3CH_2CH_2CH_2OH$$
(*B*) Butanoic acid   (*C*) Butan-1-ol

[O] ↑ CrO_3 ↓ Dehydration

$$CH_3CH_2CH=CH_2$$
But-1-ene

OR

(a) (i)
Benzene + CH_3Cl → anhyd. $AlCl_3$, Friedel−Crafts reaction

H_2O + Benzaldehyde (CHO) ← $\dfrac{CrO_2Cl_2}{\text{Etard reaction}}$ 2[O] + Toluene (CH_3)

(ii) Benzene + CH_3COCl → anhyd. $AlCl_3$, Friedel−Crafts reaction

HCl + Acetophenone ($COCH_3$)

(b) (i) C_6H_5CHO (Benzaldehyde) $\xrightarrow[\text{pH 9-10}]{NaCN/HCl}$ $C_6H_5-\overset{\overset{OH}{|}}{CH}-CN$ (Benzaldehyde cyanohydrin)

$\xrightarrow[\text{Hydrolysis}]{H^+/H_2O}$ $C_6H_5-\overset{\overset{OH}{|}}{CH}-COOH$ (α-Hydroxyphenylacetic acid)

(ii) C_6H_5Br (Bromobenzene) $\xrightarrow[\text{dry ether}]{Mg}$ C_6H_5MgBr (Phenyl magnesium bromide)

$\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CH_3CHO}$ $C_6H_5-\overset{\overset{OH}{|}}{CH}-CH_3$ (1-Phenylethanol)

(iii) Benzaldehyde (CHO) $\xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } C_6H_5MgBr}$ (CH−C_6H_5 with OH)

$\xrightarrow[\text{573 K}]{Cu}$ Benzophenone (C−C_6H_5 with O)

PRACTICE PAPER 2Q14

JEE Advanced
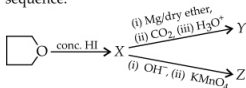
Exam on 25th May

SECTION-I
Only One Option Correct Type

This section contains 10 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. The reaction $R \longrightarrow P$, follows first order kinetics. In 60 seconds, concentration of R changes from 0.2 M to 0.05 M, then rate of reaction when concentration of R is 0.03 M is
(a) 5.44×10^{-4} M s^{-1} (b) 3.35×10^{-4} M s^{-1}
(c) 6.93×10^{-4} M s^{-1} (d) 7.89×10^{-4} M s^{-1}

2. Which of the following compounds of phosphorus contain P—O—P bond?
I.   Pyrophosphorous acid
II. Hypophosphoric acid
III. Metaphosphoric acid
IV. Orthophosphorous acid
(a) I only   (b) I and III only
(c) II and IV only   (d) III only

3. The correct decreasing order of reactivity of following compounds towards S_N2 reaction is

Br   CH$_2$Br   H$_3$C   Br   Br

(1)   (2)   (3)   (4)
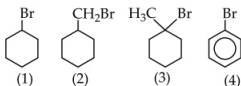
(a) $2 > 4 > 1 > 3$ (b) $3 > 1 > 2 > 4$
(c) $4 > 2 > 1 > 3$ (d) $2 > 1 > 3 > 4$

4. If excess of AgNO$_3$ solution is added to 100 mL of a 0.024 M solution of dichlorobis(ethylene diamine)cobalt(III) chloride, how many moles of AgCl will be precipitated?
(a) 1.2×10^{-3} (b) 1.6×10^{-3}
(c) 2.4×10^{-3} (d) 4.8×10^{-3}

5. Identify Y and Z in the following reaction sequence.

O ─conc. HI→ X
(i) Mg/dry ether, (ii) CO$_2$, (iii) H$_3$O$^+$ → Y
(i) OH$^-$, (ii) KMnO$_4$ → Z

	Y	Z
(a)	Succinic acid	Adipic acid
(b)	Oxalic acid	Malonic acid
(c)	Glutaric acid	Adipic acid
(d)	Adipic acid	Succinic acid

6. In the aluminothermic process, aluminium acts as
(a) an oxidising agent   (b) a flux
(c) a reducing agent   (d) a solder.

7. Which one of the following species is not a pseudohalide?
(a) CNO$^-$ (b) RCOO$^-$
(c) OCN$^-$ (d) NNN$^-$

8. In a cubic packed structure of mixed oxides, the lattice is made up of oxide ions, one-fifth of tetrahedral voids are occupied by divalent (X^{2+}) ions while one-half of the octahedral voids are occupied by trivalent ions (Y^{3+}), then the formula of the oxide is
(a) XY_2O_4 (b) X_2YO_4
(c) $X_4Y_5O_{10}$ (d) $X_5Y_4O_{10}$

9. Which of the following cations gives blood red colour with ammonium thiocyanate?
(a) Fe^{3+} (b) Fe^{2+}
(c) Cu^{2+} (d) Cd^{2+}

10. A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-18}, 10^{-24} and 10^{-53} respectively, which one will precipitate first?
(a) FeS   (b) MnS
(c) HgS   (d) ZnS

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

11. Relative stabilities of following carbocations will be in order
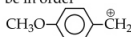
    I   II

    III   IV

  (a) I < II < III < IV   (b) IV < III < II < I
  (c) IV < II < III < I   (d) II < IV < III < I

12. Which of the following statements is/are correct for the saturated solution of salt $PbCl_2$ if its K_{sp} is 3.44×10^{-34} ?

  (a) $[Pb^{2+}]_{eq} = 4.414 \times 10^{-12}$ M
  (b) $[Cl^{-}]_{eq} = 8.828 \times 10^{-12}$ M
  (c) Solubility of salt is 4.414×10^{-12} M.
  (d) $[PbCl_2]_{eq}$ is zero.

13. Consider the following complexes:
  (1) K_2PtCl_6 (2) $PtCl_4 \cdot 2NH_3$
  (3) $PtCl_4 \cdot 3NH_3$ (4) $PtCl_4 \cdot 5NH_3$
  Their electrical conductances in aqueous solutions are
  (a) 256, 0, 97, 404   (b) 404, 0, 97, 256
  (c) 256, 97, 0, 404   (d) 404, 97, 256, 0

14. Which of the following is/are not aromatic?

  (a)   (b)

  (c)   (d)

15. Mark out the correct statement(s).
  (a) For a binary solution AB, if $F_{A-B} > F_{A-A}$ and F_{B-B}, there is negative deviation from ideality or Raoult's law.
  (b) If $F_{A-B} = F_{A-A}$ and F_{B-B} then formation of binary solution AB is not spontaneous as $\Delta H_{mixing} = 0$.
  (c) If $F_{A-B} < F_{A-A}$ and F_{B-B}, $\Delta H_{mixing} > 0$ then formation of binary solution AB is spontaneous.
  (d) There is deviation from Raoult's law in every case if $\Delta H_{mixing} \neq 0$.

Integer Value Correct Type

This section contains 5 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

16. δ-Valerolactam is x membered ring. The value of x is

17. The coordination number of the element M in the complex $M(DMG)_2$ (where DMG is dimethylglyoxime) is

18. The amount of energy required to remove the electron from Li^{2+} ion in its ground state is x times greater than the amount of energy required to remove the electron from a H-atom in its ground state. The value of x is

19. Total number of hydrogen bonds formed between Adenine and Thymine bases is

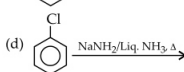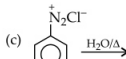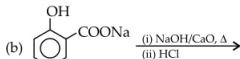20. In the following sequence of reactions, the number of asymmetric carbon atoms in D is

$$CH_3COOH \xrightarrow[]{SOCl_2} A \xrightarrow[\text{anhy. } AlCl_3]{\text{benzene}} B \xrightarrow[]{HCN} C \xrightarrow[H^+]{HOH} D$$
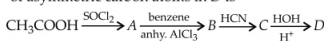
PAPER-II

One or More Options Correct Type

This section contains 8 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

1. Which of the following sets of reactions will give phenol?

  (a) $\xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) NaOH fusion}}$

  (b) $\xrightarrow[\text{(ii) HCl}]{\text{(i) NaOH/CaO, } \Delta}$

  (c) $\xrightarrow[]{H_2O/\Delta}$

  (d) $\xrightarrow[]{NaNH_2/Liq. NH_3, \Delta}$

2. Decrease in atomic number is observed in
   (a) α-emission   (b) β-emission
   (c) positron emission   (d) K-electron capture.

3. For the reaction :
   $$PCl_{5(g)} \longrightarrow PCl_{3(g)} + Cl_{2(g)}$$
   The forward reaction at constant temperature is favoured by
   (a) introducing chlorine gas at constant volume
   (b) introducing an inert gas at constant pressure
   (c) increasing the volume of the container
   (d) introducing PCl_5 at constant volume.

4. Which of the following ores is/are carbonate ore(s)?
   (a) Zincite   (b) Calamine
   (c) Siderite   (d) Sphalerite

5. Butan-2-ol is obtained by using carbonyl compound and Grignard reagent as
   (a) $CH_3CH=O$ $\xrightarrow{\text{(i) } CH_3CH_2MgBr}_{\text{(ii) } H_2O/H^+}$
   (b) $CH_3CH_2CH=O$ $\xrightarrow{\text{(i) } CH_3MgBr}_{\text{(ii) } H_2O/H^+}$
   (c) $\begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!\!\!C=O$ $\xrightarrow{\text{(i) } CH_3CH_2MgBr}_{\text{(ii) } H_2O/H^+}$
   (d) $CH_2=O$ $\xrightarrow{\text{(i) } CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-MgBr}_{\text{(ii) } H_2O/H^+}$

6. Which of the following statements is/are incorrect?
   (a) pH for 0.01 M $Ca(OH)_2$ is 12.3.
   (b) pH for 10^{-8} M NaOH is 6.
   (c) pH for 0.001 N KOH is 9.
   (d) pH for 0.008 M $Mg(OH)_2$ is 12.2.

7. The two isomers X and Y with the formula $Cr(H_2O)_5ClBr_2$ were taken for experiment on depression in freezing point. It was found that one mole of X gave depression corresponding to 2 moles of particles and one mole of Y gave depression due to 3 moles of particles. The structural formulae of X and Y respectively are
   (a) $[Cr(H_2O)_5Cl]Br_2$; $[Cr(H_2O)_4Br_2]Cl\cdot H_2O$
   (b) $[Cr(H_2O)_5Cl]Br_2$; $[Cr(H_2O)_3ClBr_2]2H_2O$
   (c) $[Cr(H_2O)_3Br]BrCl$; $[Cr(H_2O)_4ClBr]Br\cdot H_2O$
   (d) $[Cr(H_2O)_4Br_2]Cl\cdot H_2O$; $[Cr(H_2O)_5Cl]Br_2$

8. Histidine, a heterocyclic amino acid has following structure at pH < 1.82.

   [structure of histidine]
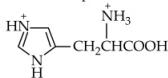
   At pH > 1.82, it should have which structure?
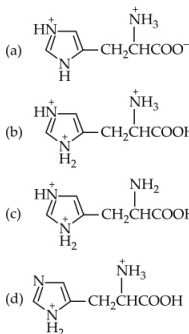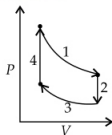
(a) [structure a]

(b) [structure b]

(c) [structure c]

(d) [structure d]

Paragraph for Questions 9 and 10

A thermodynamic process is the energetic development of a thermodynamic system proceeding from an intitial state to a final state. It can be visualized graphically by plotting the changes to the system's state variables.

[P-V diagram showing processes 1, 2, 3, 4]

In the given graph, four processes are shown. Each process has a well defined start and end point in the pressure-volume state.

9. Processes 1,2,3 and 4 are respectively
   (a) isobaric, isochoric, isobaric, isochoric
   (b) isothermal, isochoric, isobaric, isothermal
   (c) isochoric, isothermal, isochoric, isothermal
   (d) isothermal, isochoric, isothermal, isochoric.

10. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process?
   (a) For cyclic process, $q = -W$
   (b) For isochoric process, $q_v = \Delta U$
   (c) For isothermal process, $q = -W$
   (d) For isobaric process, $q_p = \Delta U$

Paragraph for Questions 11 and 12

Molecular geometries of xenon compounds are determined on the basis of VSEPR theory and concept of hybridisation.

According to this theory, the shape of the molecule is predicted by the total number of electron pairs (lone pairs + bond pairs) in the valence shell of the central xenon atom.

11. The geometry of XeO_2F_2 is
   (a) tetrahedral
   (b) square planar
   (c) trigonal bipyramidal
   (d) T-shaped.

12. Partial hydrolysis of XeF_6 gives
   (a) XeO_2F_2 (b) $XeOF_4$
   (c) XeO_3F_2 (d) $XeOF_2$

Paragraph for Questions 13 and 14

A certain metal (A) is boiled in dilute nitric acid to give a salt (B) and an oxide of nitrogen (C). An aqueous solution of (B) with brine gives a precipitate (D) which is soluble in NH_4OH. On adding the aqueous solution of (B) to hypo solution, a white precipitate (E) is obtained. (E) turns black on standing.

13. Metal (A) is
   (a) Na   (b) Be
   (c) Mg   (d) Ag

14. A white precipitate (E) is
   (a) $Na_2S_2O_3$ (b) $Ag_2S_2O_3$
   (c) MgS_2O_3 (d) $K_2S_2O_3$

Paragraph for Questions 15 and 16

Aldehydes which do not have any α-hydrogen atom when treated with a concentrated solution of NaOH or KOH, undergoes a simultaneous oxidation and reduction forming a salt of carboxylic acid and alcohol. This reaction is known as Cannizzaro reaction.

$$Ph-C-H \xrightleftharpoons{OH^-, fast} Ph-C-H + C-Ph \xrightarrow{slow}$$

$$PhCO_2^- + PhCH_2OH \xleftarrow{fast} Ph-C+H-C-Ph$$
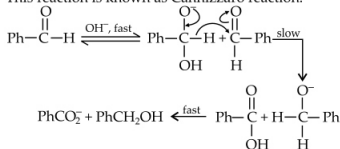
15. The Cannizaro reaction in not given by
   (a) trimethylacetaldehyde
   (b) acetaldehyde
   (c) benzaldehyde   (d) all of these.

16. In a Cannizzaro reaction, the intermediate that will be best hydride donor is

(a)   (b)

(c)   (d)
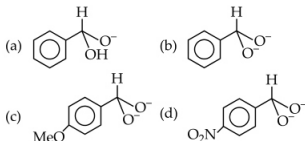
This section contains 4 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

17. Match the compounds given in the List I with their shapes given in List II and select the correct answer using the code given below the lists:

List I		List II	
P.	BO_3^{3-}	1.	Linear
Q.	I_3^-	2.	Trigonal planar
R.	O_3	3.	Tetrahedral
S.	CCl_4	4.	Bent

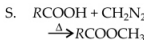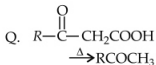|	P	Q	R	S
(a)	1	2	4	3
(b)	2	1	3	4
(c)	2	1	4	3
(d)	4	2	1	3

18. Match the reactions given in List I with their reaction intermediates given in List II and select the correct answer using the code given below the lists:

List I	List II
P. $RCOOH + N_3H$ $\longrightarrow RNH_2$	1. Six membered cyclic intermediate
Q. $R-C-CH_2COOH$ $\xrightarrow{\Delta} RCOCH_3$	2. Carbene
R. $RCH_2COOH + Br_2$ $\xrightarrow{P} RCHBrCOOH$	3. Isocyanate
S. $RCOOH + CH_2N_2$ $\xrightarrow{\Delta} RCOOCH_3$	4. Free radical

	P	Q	R	S
(a)	3	1	4	2
(b)	2	1	3	4
(c)	3	4	1	2
(d)	4	1	3	2

19. Match the terms given in List I with appropriate values given in List II and select the correct answer using the code given below the lists :

List I		List II	
P.	Oxidation potential of hydrogen electrode set up in a solution with pH = 2.	1.	0.018 V
Q.	Oxidation potential of hydrogen electrode set up in 0.5 M HCl solution.	2.	0.059 V
R.	EMF of concentration cell with hydrogen electrodes set up in 0.01 M and 0.1 M HCl solutions.	3.	0.035 V
S.	EMF of concentration cell with hydrogen electrodes set up in 0.1 M and 0.4 M HCl solutions.	4.	0.118 V

```
      P   Q   R   S
(a)   1   3   2   4
(b)   4   1   2   3
(c)   3   1   4   2
(d)   3   2   4   1
```

20. Match the reactions given in List I with their types given in List II and select the correct answer using the code given below the lists :

List I		List II	
P.	$2H_2O \xrightarrow{\Delta}$ $2H_2 + O_2$	1.	Disproportionation reaction
Q.	$CuSO_4 + Zn \longrightarrow$ $Cu + ZnSO_4$	2.	Non-metal displacement reaction
R.	$Cl_2 + 6OH^- \xrightarrow{\Delta}$ $5Cl^- + ClO_3^- + 3H_2O$	3.	Decomposition reaction
S.	$Zn + 2HCl \longrightarrow$ $ZnCl_2 + H_2$	4.	Metal displacement reaction

```
      P   Q   R   S
(a)   3   4   2   1
(b)   2   3   4   1
(c)   3   4   1   2
(d)   2   1   3   4
```
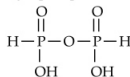
SOLUTIONS

PAPER-I

1. **(c) :** Since the reaction $R \longrightarrow P$, follows first order kinetics

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{60} \log \frac{0.2}{0.05} = 2.3 \times 10^{-2} s^{-1}$$

Rate $= k[R]$
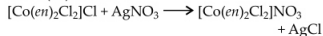$= 2.31 \times 10^{-2} \times 0.03 = 6.93 \times 10^{-4}$ M s^{-1}

2. **(b):** I. Pyrophosphorous acid :

II. Hypophosphoric acid : $HO-\overset{\overset{O}{\|}}{\underset{OH}{P}}-\overset{\overset{O}{\|}}{\underset{OH}{P}}-OH$

III. Metaphosphoric acid :

IV. Orthophosphorous acid : $H-\overset{\overset{O}{\|}}{\underset{OH}{P}}-OH$
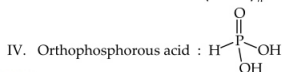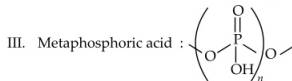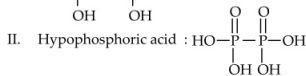
3. **(d):** Nucleophilic substitution through S_N2 mechanism is governed by steric hindrance. Thus reactivity of
$1° RX > 2° RX > 3° RX >$ aryl halide
$\therefore 2 > 1 > 3 > 4$

4. **(c) :** Moles of the complex $= \frac{100 \times 0.024}{1000}$
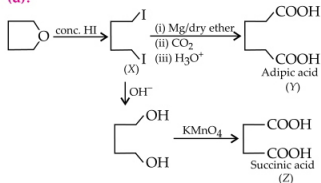$= 2.4 \times 10^{-3}$ mol
Complex is dichlorobis(ethylenediamine) cobalt(III) chloride.
$[Co(en)_2Cl_2]Cl + AgNO_3 \longrightarrow [Co(en)_2Cl_2]NO_3 + AgCl$
Since one mole of AgCl is formed per mole of complex.
Moles of AgCl precipitated $= 2.4 \times 10^{-3}$ mol

5. **(d):**

6. **(c) :** Aluminium reduces Fe_2O_3/Cr_2O_3 to Fe/Cr and itself gets oxidised to Al_2O_3. Thus, Al acts as a reducing agent.
$Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3$

7. **(b):** Pseudohalides are monovalent ions made by an electronegative atom and have properties similar to those of halide ions. The corresponding dimers of pseudohalides are known as pseudohalogens. $RCOO^-$ is not a pseudohalide.

8. **(c)** : In ccp, anions occupy primitives of the cube while cations occupy voids. In ccp there are two tetrahedral voids and one octahedral hole per anion.

For one oxygen atom there are two tetrahedral holes and one octahedral hole.

Since one-fifth of the tetrahedral voids are occupied by divalent cations (X^{2+}).

∴ Number of divalent cations in tetrahedral voids $= 2 \times \dfrac{1}{5}$

Since one-half of the octahedral voids are occupied by trivalent cations (Y^{3+})

∴ Number of trivalent cations $= 1 \times \dfrac{1}{2}$

So, the formula of the compound is $(X)_{2 \times \frac{1}{5}} (Y)_{1 \times \frac{1}{2}} (O)_1$ or $X_{\frac{2}{5}} Y_{\frac{1}{2}} O_1$ or $X_4 Y_5 O_{10}$.

9. **(a)** : $Fe^{3+} + 3SCN^- \longrightarrow \underset{\text{Blood red colour}}{Fe(SCN)_3}$

10. **(c)** : $[S^{2-}]$ needed for precipitation of

$MnS = \dfrac{10^{-13}}{10^{-3}} = 10^{-10} M$

$FeS = \dfrac{10^{-18}}{10^{-3}} = 10^{-15} M$

$ZnS = \dfrac{10^{-24}}{10^{-3}} = 10^{-21} M$

$HgS = \dfrac{10^{-53}}{10^{-3}} = 10^{-50} M$

Thus, minimum $[S^{2-}]$ is for HgS and so it will be precipitated first.

11. **(c)** : Electron releasing group increases the stability of carbocation. $+R$ effect of CH_3O- group dominates over $-I$ effect hence, it is a electron donating group.

$+R$ effect of CH_3O- group is greater than $+I$ effect of CH_3- group.

Benzyl carbocation is more stabilised than ethyl carbocation due to resonance. Thus, the stability order is IV < II < III < I.

12. **(a,b,c,d)** : $PbCl_2 \rightleftharpoons \underset{s}{Pb^{2+}} + \underset{2s}{2Cl^-}$

Let s be the solubility of $PbCl_2$.

$K_{sp} = [Pb^{2+}][Cl^-]^2 = 4s^3$

$s = \sqrt[3]{\dfrac{3.44 \times 10^{-34}}{4}} = 4.414 \times 10^{-12} M$

$[Pb^{2+}]_{eq} = 4.414 \times 10^{-12} M$

$[Cl^-]_{eq} = 2 \times 4.414 \times 10^{-12} = 8.828 \times 10^{-12} M$

$[PbCl_2]_{eq} = 0$, because the salt is completely ionised.

13. **(a)** : (1) $K_2[PtCl_6] \rightleftharpoons 2K^+ + [PtCl_6]^{2-}$, No. of ions = 3
(2) $PtCl_4 \cdot 2NH_3$, $[Pt(NH_3)_2Cl_4]$, No. of ions = 0

(3) $PtCl_4 \cdot 3NH_3$, $[Pt(NH_3)_3Cl_3]Cl$, No. of ions = 2
(4) $PtCl_4 \cdot 5NH_3$, $[Pt(NH_3)_5Cl]Cl_3$, No. of ions = 4

More the number of ions, more is the conductance. Thus, the order of their electrical conductances is (4) > (1) > (3) > (2).

14. **(a,d)** : Both (a) and (d) have 8π electrons which is not equal to $(4n + 2)\pi$. Hence, they do not obey Huckel's rule of aromaticity.

15. **(a,d)** : Stronger resultant molecular attraction (F_{A-B}) results in negative deviation and $\Delta H_{mix} < 0$. Weaker resultant force (F_{A-B}) results in positive deviation and $\Delta H_{mix} > 0$.
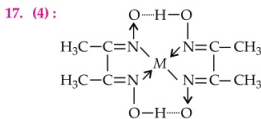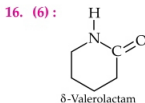
For an ideal solution, $\Delta H_{mix} = 0$.

Thus, $\Delta G_{mix} = -T\Delta S_{mix}$ ($\because \Delta S_{mix} > 0$)
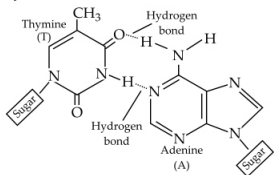
$\Delta G_{mix} = -ve$

Hence, formation of binary solution AB is spontaneous.

If the solute-solvent forces of attraction are weaker than individual solute and solvent intermolecular attractions, then solute will not dissolve. Hence, formation of binary solution AB is non-spontaneous.
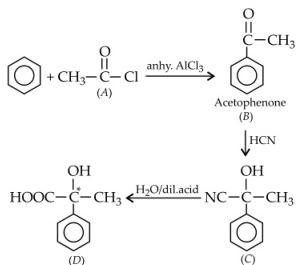
16. **(6)** :

δ-Valerolactam

17. **(4)** :

18. **(9)** : $E_{Li^{2+}} = E_H \times Z^2 = E_H \times (3)^2 = 9E_H$

19. **(2)** : Adenine makes two hydrogen bonds with Thymine.

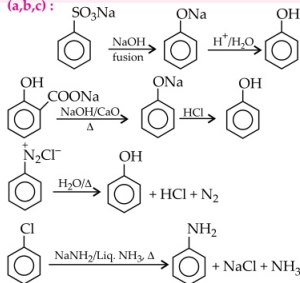20. **(1)** : $CH_3-COOH \xrightarrow{SOCl_2} \underset{(A)}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} + SO_2\uparrow + HCl$

$$\text{benzene} + CH_3-\underset{\overset{\|}{O}}{C}-Cl \xrightarrow{\text{anhy. AlCl}_3} \text{Acetophenone}$$

(A) ... (B)

$$\downarrow HCN$$

$$HOOC-\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xleftarrow{H_2O/\text{dil. acid}} NC-\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

(D) ... (C)

PAPER-II

1. (a,b,c) :

2. (a,c,d) : α-emission : $^m_z A \longrightarrow ^{m-4}_{z-2}B + ^4_2He$;

(z decreases)

β-emission : $^m_z A \longrightarrow ^m_{z+1}B + ^0_{-1}e$; (z increases)

Positron emission : $^1_1p \longrightarrow ^1_0n + ^0_{+1}e$; (z decreases)

K-electron capture : $^1_1p + ^0_{-1}e \longrightarrow ^1_0n + X\text{-ray}$; (z decreases)

3. (b,c,d) : If we introduce an inert gas at constant pressure then the equilibrium is shifted in the direction in which the number of moles increases. Also the forward reaction is accelerated by increase in quantity of PCl_5 (a reactant) and by increase of space (i.e. volume of container) which will decrease the pressure. Introducing Cl_2 gas at constant volume will shift the reaction in backward direction.

4. (b,c) : Zincite = ZnO
Calamine : $ZnCO_3$
Siderite : $FeCO_3$
Sphalerite : ZnS

5. (a, b) :
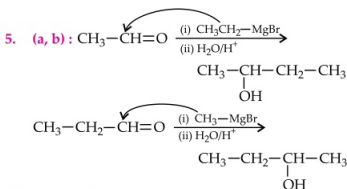
6. (c) : (a) pH for 0.01 M $Ca(OH)_2$,
$[OH^-] = 2 \times 0.01 = 0.02$ M
$pOH = -\log[OH^-] = -\log(0.02) = 1.6989$
$pH = 14 - pOH = 14 - 1.6989 = 12.3$
(b) pH for 10^{-8} M NaOH,
$[OH^-] = 10^{-8}$ M
$pOH = -\log[OH^-] = -\log(10^{-8}) = 8$
$pH = 14 - pOH = 14 - 8 = 6$
(c) pH for 0.001 N KOH,
since, KOH is monovalent, Normality = Molarity
$[OH^-] = 0.001$ M $= 10^{-3}$ M
$pOH = -\log[OH^-] = -\log(10^{-3}) = 3$
$pH = 14 - pOH \Rightarrow pH = 14 - 3 = 11$
(d) pH for 0.008 M $Mg(OH)_2$,
$[OH^-] = 2 \times 0.008 = 0.016$ M
$pOH = -\log[OH^-] = -\log(0.016) = 1.7959$
$pH = 14 - pOH = 14 - 1.7959 = 12.2$

7. (d): X gave depression corresponding to 2 moles of particles.
$X, [Cr(H_2O)_4Br_2]Cl \cdot H_2O \rightleftharpoons [Cr(H_2O)_4Br_2]^+ + Cl^-$
Y gave depression corresponding to 3 moles of particles.
$Y, [Cr(H_2O)_5Cl]Br_2 \rightleftharpoons [Cr(H_2O)_5Cl]^{2+} + 2Br^-$

8. (a): On increasing the pH by adding an alkali, H^+ will be lost from $-COOH$.

9. (d): Processes 1 and 3 are isothermal as pressure is continuously decreasing with increase in volume (1) and increasing with decrease in volume (3). This is possible only at constant temperature (Boyle's law).
While processes 2 and 4 are isochoric as volume is constant.

10. (d): For isobaric process, $q_p = \Delta H$

11. (c) :

XeO_2F_2
Trigonal bipyramidal

12. (b): $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$

13. (d): Compound (B) gives white precipitate (D) with NaCl (brine), soluble in NH_4OH hence it should be AgCl, (B) must contain Ag^+ ions, *i.e.*, metal (A) is silver.

Reactions :

$$\underset{(A)}{3Ag} + 4HNO_3 \text{ (dil.)} \longrightarrow \underset{(B)}{3AgNO_3} + \underset{(C)}{NO} + 2H_2O$$

$$\underset{(B)}{AgNO_3} + NaCl \longrightarrow \underset{(D)}{AgCl\downarrow} + NaNO_3$$

$$\underset{(D)}{AgCl} + 2NH_4OH \longrightarrow \underset{(Soluble)}{[Ag(NH_3)_2]Cl} + 2H_2O$$

14. (b): $2AgNO_3 + Na_2S_2O_3 \longrightarrow \underset{(E)\ (White)}{Ag_2S_2O_3\downarrow} + 2NaNO_3$

$$\underset{(E)}{Ag_2S_2O_3} + H_2O \longrightarrow \underset{(Black)}{Ag_2S\downarrow} + H_2SO_4$$

15. (b) :

Cannizzaro reaction is given by only those aldehydes which do not have α-hydrogen atom. Thus, acetaldehyde (b) will not give Cannizzaro reaction.

16. (c) :

Due to the presence of electron donating methoxy group (–OMe) at the *p*-position, the removal of hydride ion (: H^-) is facilitated.

17. (c) :

18. (a): P :

Q :

R : $R-CH_2COOH \xrightarrow{Br_2/P} RCH_2COBr$;

$Br_2 \xrightarrow{\Delta} 2B\dot{r}$

$RCH_2COBr + B\dot{r} \rightleftharpoons R-\dot{C}HCOBr \xrightarrow{Br_2}$

S :

19. (b): P : $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

$$E_{H^+/\frac{1}{2}H_2} = E^\circ - \frac{0.059}{1}\log\frac{1}{[H^+]}$$

$$= 0 - 0.059 \text{ pH} = -0.059 \times 2 = -0.118 \text{ V}$$

∴ Oxidation potential = 0.118 V

Q : $E_{H^+/\frac{1}{2}H_2} = -\frac{0.059}{1}\log\frac{1}{0.5}$

$$= -0.059 \log 2 = -0.018 \text{ V}$$

∴ Oxidation potential = 0.018 V

R : $E_{cell} = \frac{0.059}{1}\log\frac{c_2}{c_1}$

$$= 0.059 \log\frac{0.1}{0.01} = 0.059 \text{ V}$$

S : $E_{cell} = \frac{0.059}{1}\log\frac{0.4}{0.1}$

$$= 0.059 \log 4 = 0.035 \text{ V}$$

20. (c): P : $2H_2O \xrightarrow{\Delta} 2H_2 + O_2$ is a decomposition reaction.

Q : $CuSO_4 + Zn \longrightarrow Cu + ZnSO_4$ is a metal displacement reaction.

R : $Cl_2 + 6OH^- \xrightarrow{\Delta} 5Cl^- + ClO_3^- + 3H_2O$ is a disproportionation reaction.

S : $Zn + 2HCl \longrightarrow ZnCl_2 + H_2$ is a non-metal displacement reaction.

■■

CHEMISTRY MUSING

1. (d) : Mass of acetic acid = 3×10^{-3} kg = 3 g

No. of moles of acetic acid,

$$n_2 = \frac{3 \text{ g}}{60 \text{ g mol}^{-1}} = 0.05 \text{ mol}$$

Volume of water, $V = 500$ cm^3

Mass of water, $w_1 = V\rho = (500 \text{ cm}^3)(0.997 \text{ g cm}^{-3})$
$$= 498.5 \text{ g} = 0.4985 \text{ kg}$$

Molality of acetic acid,

$$m = \frac{n_2}{w_1} = \frac{0.05 \text{ mol}}{0.4985 \text{ kg}} = 0.1003 \text{ mol kg}^{-1}$$

Since 23% of acetic acid is dissociated, its degree of dissociation (α) will be 0.23. Hence, in solution we have

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$(1-\alpha) \qquad\qquad \alpha \qquad \alpha$$
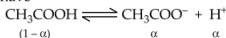
The total no. of species in solution,

$$i = (1-\alpha) + \alpha + \alpha = (1+\alpha)$$

As, $\Delta T_f = iK_f m$ $\therefore$ $\Delta T_f = (1+\alpha) K_f m$

$= (1 + 0.23)1.86 \text{ K kg mol}^{-1} (0.1003 \text{ mol kg}^{-1}) = 0.23$ K

2. (b) :
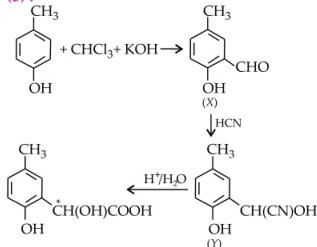
3. (a) : Carbon monoxide is oxidised to carbon dioxide by passing the gases with steam over iron chromate as catalyst at 673 K resulting in the production of more H_2.

$$CO_{(g)} + H_2{(g)} + H_2O{(g)} \xrightarrow[673 \text{ K}]{FeCrO_4} CO_{2(g)} + 2H_2{(g)}$$
$$\text{Water gas} \qquad\qquad\qquad \text{Syn gas}$$
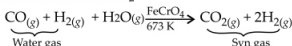
This conversion of water gas into syn gas is called water gas shift reaction. CO_2 is absorbed in alkali.

$$CO_2 + NaOH \longrightarrow NaHCO_3$$
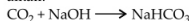
4. (c) : Amongst the given compounds the K_{sp} of HgS is minimum, so it will get precipitated first.

5. (c) : $C_{rms} = \sqrt{\dfrac{3RT}{M}}$, $\dfrac{C_{rms}(H_2)}{C_{rms}(N_2)} = \sqrt{\dfrac{T(H_2)}{T(N_2)} \times \dfrac{M(N_2)}{M(N_2)}}$

$$\sqrt{7} = \sqrt{\frac{T(H_2)}{T(N_2)} \times \frac{28}{2}} \text{ or, } \frac{T(H_2)}{T(N_2)} = \frac{1}{2}$$

6. (a) :
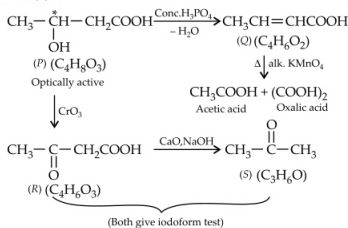
7. (b) : Chalcopyrite is converted into cuprous sulphide and ferrous sulphide with evolution of sulphur dioxide.

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$
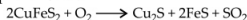
Then sulphides of copper and iron are partially oxidised. (Roasting)

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
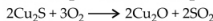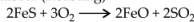
8. (c) : $Cu_2\overset{-2}{S} + 2Cu_2O \longrightarrow 6Cu + \overset{+4}{S}O_2$

Thus, S^{2-} gets oxidised to S^{4+} i.e., SO_2 and reduces Cu^{2+} to Cu.

9. (7) : Given that, $K.E. = 4.55 \times 10^{-25}$ J,
$h = 6.6 \times 10^{-34}$ kg m^{2}s^{-1}, $m = 9.1 \times 10^{-31}$ kg

$$V = \sqrt{\frac{2 \times K.E.}{m}} = \sqrt{\frac{2 \times 4.55 \times 10^{-25}}{9.1 \times 10^{-31}}} = 10^3 \text{ m s}^{-1}$$

$$\lambda = \frac{h}{mV} = \frac{6.6 \times 10^{-34}}{9.1 \times 10^{-31} \times 10^3} = 7.25 \times 10^{-7} \text{ m}$$

10. (5) : The possible cyclic isomers of the compound with molecular formula C_4H_6 are

ASSERTION & REASON

Directions : Mark the correct choice as:

(a) If both assertion and reason are true and reason is the correct explanation of assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of assertion.

(c) If assertion is true but reason is false.

(d) If both assertion and reason are false.

PHYSICAL CHEMISTRY

1. **Assertion :** Schottky defect does not affect the density of the substance.
   Reason : Schottky defect arises when some constituent particles occupy an interstitial site.

2. **Assertion :** In the ground state of the atoms, the orbitals are filled in order of their increasing energies.
   Reason : The order of increasing energies of the various orbitals is given by $(n + l)$ rule.

3. **Assertion :** For the first order reaction, half-life period is expressed as
   $$t_{1/2} = \frac{2.303}{k} \log 2$$
   Reason : The half-life time of a first order reaction is not always constant and it depends upon the initial concentration of reactants.

4. **Assertion :** Gases do not liquefy above their critical temperature even on applying high pressure.
   Reason : Above critical temperature, the molecular speed is high and intermolecular attractions cannot hold the molecules together because they escape due to high speed.

5. **Assertion :** Decrease in the vapour pressure of water by adding 1.0 mol of sucrose to one kg of water is nearly similar to that produced by adding 1.0 mol of urea to the same quantity of water at the same temperature.
   Reason : Decrease in the vapour pressure of solvent depends on the quantity of non-volatile solute present in the fixed amount of solvent, irrespective of its nature.

6. **Assertion :** Nitrogen (28 parts) forms five stable oxides with oxygen containing 16, 32, 48, 64 and 80 parts respectively. This data illustrates the law of multiple proportions.
   Reason : According to law of multiple proportions, the relative amounts of an element combining with some fixed amount of a second element in a series of compounds are the ratios of simple whole numbers.

7. **Assertion :** Molar conductivity for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.
   Reason : For weak electrolytes, degree of dissociation increases with dilution of solution.

8. **Assertion :** The order of bond lengths of O_2^+, O_2^{2-}, O_2 and O_2 is
   $$O_2^{2-} > O_2^- > O_2 > O_2^+$$
   Reason : O_2, O_2^+ and O_2^- are diamagnetic while O_2^{2-} is paramagnetic.

9. **Assertion :** Addition of an inert gas at constant volume shifts the equilibrium towards lesser number of moles.
   Reason : Addition of an inert gas at constant pressure does not affect the equilibrium.

10. **Assertion :** A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic.

    Reason : All exothermic reactions are accompanied by decrease of randomness.

ORGANIC CHEMISTRY

11. **Assertion :** The observed order of carbocation stability is

    $(CH_3)_3\overset{+}{C} < (CH_3)_2\overset{+}{C}H < CH_3\overset{+}{C}H_2 < \overset{+}{C}H_3$

    Reason : Alkyl groups directly attached to the positively charged carbon destabilise the carbocations.

12. **Assertion :** Ethane, ethene and ethyne follow the order of their acidic behaviour as Ethyne > Ethene > Ethane

    Reason : Hydrogen atoms in ethyne are attached to the sp hybridised carbon atoms whereas they are attached to sp^2 hybridised carbon atoms in ethene and sp^3 hybridised carbon atoms in ethane.

13. **Assertion :** 1-Butene on reaction with HBr in the presence of peroxide produces 1-bromobutane.

    Reason : It involves formation of a primary radical.

14. **Assertion :** Boiling point of propan-1-ol (370 K) is higher than that of methoxyethane (281 K) though they have same molecular mass (60).

    Reason : The higher boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers.

15. **Assertion :** Acetoacetic ester $(CH_3COCH_2COOC_2H_5)$ contains CH_3CO—group but does not give iodoform test.

    Reason : The H-atoms of the CH_3— group are more acidic than those of —CH_2— group.

16. **Assertion :** The basicity order of aliphatic amines, aromatic amines and ammonia follows:

    Aliphatic amines > Ammonia > Aromatic amines

    Reason : Aliphatic amines are stronger bases than ammonia due to −I effect of alkyl groups whereas aromatic amines are weaker bases than ammonia due to +I effect of aryl group.

17. **Assertion :** A solution of sucrose in water is dextrorotatory. But on hydrolysis in the presence of a little hydrochloric acid, it becomes laevorotatory.

    Reason : Sucrose on hydrolysis gives unequal amounts of glucose and fructose. As a result of this, change in sign of rotation is observed.

18. **Assertion :** Bakelite is a thermosetting plastic.

    Reason : In thermosetting plastics, the polymeric chains are held together by strong ionic bonds.

19. **Assertion :** Phenol undergoes Kolbe reaction whereas ethanol does not.

    Reason : Phenoxide ion is more basic than ethoxide ion.

20. **Assertion :** Chloroacetic acid is a stronger acid than acetic acid.

    Reason : Chlorine atom because of its +I effect, destabilises the chloroacetate ion as compared to acetate ion by dispersing the negative charge.

INORGANIC CHEMISTRY

21. **Assertion :** Water containing soluble chlorides and sulphates of Ca and Mg is called permanent hard water.

    Reason : Permanent hardness can be removed by Clark's method.

22. **Assertion :** Lewis acid character of boron trihalides decreases in the order: $BF_3 > BCl_3 > BBr_3 > BI_3$.

    Reason : As electronegativity increases from F to I, Lewis acid character decreases from BF_3 to BI_3.

23. **Assertion :** The basic strength of alkali metal hydroxides increases as we go down the group from LiOH to CsOH.

    Reason : The hydroxides of alkali metals have low ionization energies which decrease down the group.

24. Assertion : Gold is recovered from its solution containing aurocyanide complex by adding zinc dust.

    Reason : Zinc is more electropositive than gold.

25. Assertion : Hydrides of group 16 elements show volatility in the order :
$H_2O > H_2S > H_2Se > H_2Te$
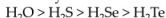
    Reason : Electronegativity of group 16 increases down the group from oxygen to tellurium.

26. Assertion : Cuprous ion (Cu⁺) is colourless whereas cupric ion (Cu^{2+}) is blue in the aqueous solution.

    Reason : Cuprous ion (Cu⁺) has unpaired electrons while cupric ion (Cu^{2+}) does not have.

27. Assertion : Lanthanoids show a limited number of oxidation states whereas actinoids show a large number of oxidation states.

    Reason : Energy gap between $4f$, $5d$ and $6s$ sub-shells is small whereas that between $5f$, $6d$ and $7s$ sub-shells is large.

28. Assertion : Complexes $K_4[Fe(CN)_6]$ and $[Co(NH_3)_5(CO_3)]Cl$ do not show geometrical isomerism.

    Reason : Geometrical isomerism is not shown by complex $[Pt(NH_3)(Cl)(py)(Br)]$.

29. Assertion : PbI_4 is stronger reducing agent than SnI_4.

    Reason : Stability of higher oxidation states increases down the group from C to Pb.

30. Assertion : H_2S is stronger acid than PH_3.

    Reason : S is more electronegative than P, conjugate base HS⁻ is more stable than H_2P^-.

SOLUTIONS

1. (d): Schottky defect decreases the density of the substance. It is a vacancy defect in ionic solids, in which number of missing cations and anions are equal in order to maintain electrical neutrality.

2. (b): Electrons enter into higher energy orbitals only when the lower energy orbitals are filled. The energy of an orbital depends on the sum of n and l. Lower the value of ($n + l$) for an orbital, lower is its energy. In case of two different types of orbitals having same value of ($n + l$), the orbital

with lower value of n has lower energy.

3. (c) : For a first order reaction, $k = \dfrac{2.303}{t} \log \dfrac{a}{a-x}$

$$k = \dfrac{2.303}{t_{1/2}} \log \dfrac{a}{a-a/2} = \dfrac{2.303}{t_{1/2}} \log \dfrac{a}{a/2} = \dfrac{2.303}{t_{1/2}} \log 2$$

Therefore, half-life period $t_{1/2} = \dfrac{2.303}{k} \log 2$

Thus $t_{1/2}$ is independent of initial concentration of reactants for first order reaction.

4. (a)   **5. (a)**

6. (a) :

Nitrogen	Oxygen	Oxides
28 parts	16 parts	N_2O
28 parts	32 parts	N_2O_2
28 parts	48 parts	N_2O_3
28 parts	64 parts	N_2O_4
28 parts	80 parts	N_2O_5

The masses of oxygen which combine with same mass of nitrogen in the five different oxides bear a ratio of $1 : 2 : 3 : 4 : 5$.

7. (a)

8. (c) : $O_2 : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$
$$(\pi 2p_x^2 = \pi 2p_y^2), (\pi^* 2p_x^1 = \pi^* 2p_y^1)$$

Bond order $= \dfrac{1}{2}(10 - 6) = 2$

Paramagnetic
$O_2^+ : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$
$$(\pi 2p_x^2 = \pi 2p_y^2), \pi^* 2p_x^1$$

Bond order $= \dfrac{1}{2}(10 - 5) = 2.5$

Paramagnetic
$O_2^- : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2,$
$$(\pi 2p_x^2 = \pi 2p_y^2), (\pi^* 2p_x^2 = \pi^* 2p_y^1)$$

Bond order $= \dfrac{1}{2}(10 - 7) = 1.5$

Paramagnetic
$O_2^{2-} : \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, (\pi 2p_x^2 = \pi 2p_y^2),$
$$(\pi^* 2p_x^2 = \pi^* 2p_y^2)$$

Bond order $= \dfrac{1}{2}(10 - 8) = 1$

Diamagnetic
Greater is the bond order, smaller is the bond length.

9. (d): Addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substances involved in the reaction. Thus, equilibrium will remain undisturbed. Addition of an inert gas at constant pressure shifts the equilibrium towards larger number of moles as volume increases to keep the pressure constant.

10. **(c)** : $\Delta G = \Delta H - T\Delta S$
   As the reaction is accompanied by decrease in randomness,
    $\Delta G = \Delta H + T\Delta S$ [$\because \Delta S$ is negative]
    For reaction to be spontaneous ΔG should be negative which is possible only if reaction is highly exothermic *i.e* ΔH is negative.
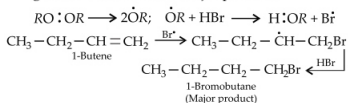   Exothermic reactions may be accompanied by increase or decrease of randomness.

11. **(d):** Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects.
    Hence, the observed order of carbocation stability is
    $$\overset{+}{C}H_3 < CH_3\overset{+}{C}H_2 < (CH_3)_2\overset{+}{C}H < (CH_3)_3\overset{+}{C}$$
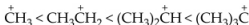
12. **(a):** Due to the maximum percentage of s character (50%), the sp hybridised orbitals of carbon atoms in ethyne have highest electronegativity; hence, these attract the shared pair of electrons of the C—H bond to a greater extent than that of the sp^2 hybridised orbitals of carbon atoms in ethene and sp^3 hybridised orbitals of carbon atoms in ethane. Thus in ethyne, hydrogen atoms can be liberated as protons more easily as compared to ethene and ethane.

13. **(c)** : As 2° free radical is more stable than 1° free radical, 1-butene on reaction with HBr in the presence of peroxide gives secondary free radical which takes hydrogen free radical from HBr to give 1-bromobutane as major product.
    $$RO \colon OR \longrightarrow 2\dot{O}R; \quad \dot{O}R + HBr \longrightarrow H \colon OR + B\dot{r}$$
    $$CH_3 - CH_2 - CH = CH_2 \xrightarrow{B\dot{r}} CH_3 - CH_2 - \dot{C}H - CH_2Br$$
    $$\underset{\text{1-Butene}}{} \qquad\qquad \xleftarrow{HBr} CH_3 - CH_2 - CH_2 - CH_2Br$$
    $$\underset{\substack{\text{1-Bromobutane} \\ \text{(Major product)}}}{}$$

14. **(a)**

15. **(c)** : The H-atoms of the $-CH_2-$ group are more acidic than those of CH_3- group.

16. **(c)** : Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups whereas aromatic amines are weaker bases than ammonia due to delocalization of lone pair of electrons present on nitrogen atom over benzene ring.

17. **(c)** : The hydrolysis of sucrose by boiling with a mineral acid (HCl), produces a mixture of equal amounts of D-glucose and D-fructose. Sucrose solution is dextrorotatory, specific rotation = + 66.5°. But on hydrolysis, it becomes laevorotatory. The specific rotation of D-glucose

is + 52.5° and of D-fructose is −92.4°. Therefore, the net specific rotation of an equimolar mixture of both is
$$\frac{+52.5° - 92.4°}{2} = -19.95°$$
$\therefore$ Laevorotatory

18. **(c)** : Thermosetting plastics are cross-linked high polymers formed from their monomers by condensation polymerization. In these polymers the chains are held together by strong covalent bonds. Bakelite is also a condensation polymer and formed by condensation polymerization of formaldehyde and phenol.

19. **(c)** : Phenol is acidic in nature because phenoxide ion formed after ionisation is highly stable as the negative charge is delocalised due to resonance.
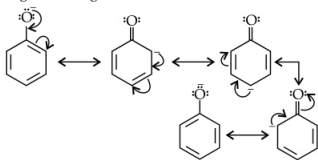
As phenoxide ion is highly stable it will act as weak base.

20. **(c)** : Because of –I effect of chlorine atom, it facilitates the release of H$^+$ ion by making O – H bond weaker. It also stabilises the chloroacetate ion by dispersing the negative charge.
    As a result of these two effects, chloroacetic acid is a stronger acid than acetic acid.
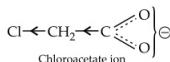
21. **(c)** : Permanent hardness is due to the presence of soluble salts of Mg and Ca in the form of chlorides and sulphates in water. It can be removed by special methods like washing soda method, Calgon's method, ion exchange method and synthetic resin method.

22. **(d):** Lewis acid character of boron trihalides follows the order: $BI_3 > BBr_3 > BCl_3 > BF_3$.

This order can be easily explained on the basis of the tendency of the halogen atom to back donate its lone pair of electrons to the boron atom through $p\pi - p\pi$ bonding which results in decrease in Lewis acid character.

The tendency to form $p\pi - p\pi$ bond is maximum in the case of BF_3 due to identical size of $2p$ orbitals of F and B atoms and falls rapidly as we move from BCl_3 to BI_3.

23. **(a) :** Due to low ionization energies of alkali metal hydroxides, the $M - O$ bond in $M - OH$ can easily break giving M^+ and OH^- ions.

$MOH \rightarrow M^+ + OH^-$ (basic nature)
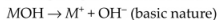
The ionization energy decreases as we go down the group. So $M - OH$ bond is more and more easily cleaved and the basic strength increases down the group from LiOH to CsOH.

24. **(a) :** This method is known as Mac-Arthur Forest cyanide process. Gold particles dissolve in dilute solution of sodium cyanide in presence of oxygen of the air forming complex cyanides.

$4Au + 8NaCN + 2H_2O + O_2 \rightarrow$
$\qquad\qquad\qquad 4Na[Au(CN)_2] + 4NaOH$
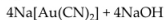
Gold is recovered from the solution by the addition of electropositive metal.

$2Na[Au(CN)_2] + Zn \rightarrow \underset{\text{Soluble complex}}{Na_2[Zn(CN)_4]} + 2Au\downarrow$
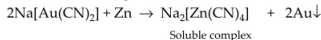
25. **(d) :** Hydrides of group 16 elements show volatility in the order :

$H_2S > H_2Se > H_2Te > H_2O$
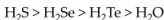
Oxygen is most electronegative than other elements of group 16, it undergoes hydrogen bonding. Due to strong intermolecular hydrogen bonding in H_2O, it shows lowest volatility.

As the size of the atom increases regularly from sulphur to tellurium, van der Waals' forces of attraction increase and hence volatility decreases from H_2S to H_2Te.

26. **(c) :** Cuprous ion (Cu^+) is colourless because it does not have unpaired electrons in the $3d$ sub-shell as it has $3d^{10}$ configuration. The cupric ion (Cu^{2+}) has one unpaired electron as it has $3d^9$ configuration. By absorbing the visible light, the unpaired electron can undergo d-d-transition under the applied field of water molecules. Hence, cupric ion (Cu^{2+}) in aqueous solution shows blue colour.

27. **(c) :** Energy gap between $4f$, $5d$ and $6s$ sub-shells is large whereas gap between $5f$, $6d$ and $7s$ sub-shells is small.

28. **(c) :** Complexes of type Ma_6 and Ma_5b (where a and b are unidentate ligands) do not show geometrical isomerism because change of position of ligands gives the same arrangement.

Complex of type $Mabcd$ (where a, b, c and d are unidentate ligands) exists in three isomeric forms which are obtained by selecting one ligand (e.g. a) and placing the remaining three ligands (e.g. b, c, d) one by one, trans to ligand a.

29. **(d):** Due to inert pair effect, stability of lower oxidation states increases down the group from carbon to lead.

Thus, lead compounds in +2 oxidation state are stable and in +4 oxidation state are strong oxidising agents.

30. **(a) :** $H_2S_{(g)} + aq \longrightarrow HS^-_{(aq)} + H^+_{(aq)}$

$\qquad PH_{3(g)} + aq \longrightarrow H_2P^- + H^+_{(aq)}$

As S is more electronegative than P, conjugate base HS^- is more stable than H_2P^-. Hence, H_2S is stronger acid than PH_3.

CONCEPT BOOSTER

Some evidences that decide whether a particular nucleophilic substitution is S_N1 or S_N2 in nature:

1. Kinetics of the reactions and rate law expression

S_N2: On changing the concentration of the substrate and nucleophile, experimentally it has been observed that the rate of an S_N2 reaction changes. This observation confirms that there is a transition state in S_N2 reaction and it is a concerted process i.e. both the substrate and the nucleophile are involved in the rate determining step (RDS). However, this is not a very strong evidence, as there may be many possible paths for the following rate law expression.

Rate = k [alkyl halide][nucleophile]

S_N1: Evidence through kinetics and rate law expression is stronger in case of S_N1.

It is believed that S_N1 reaction is a multi-step process (in fact, two step process) in which steps are:

Step-1: $R - X \xrightarrow{\text{slow}} R^+ + \overset{\cdot\cdot}{X}$

Step-2: $R^+ + \overset{\cdot\cdot}{Nu} \xrightarrow{\text{fast}} R-Nu$
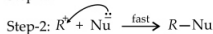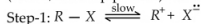
The leaving group i.e. $\overset{\cdot\cdot}{X}$ resides in the nearby area only and with the progress of the reaction concentration of $\overset{\cdot\cdot}{X}$ increases. Due to the common ion effect, backward reaction is promoted now. Even if from outside, we add a bit of $\overset{\cdot\cdot}{X}$, rate of the reaction is found to decrease. This is because with the increase in $\overset{\cdot\cdot}{X}$, reestablishment of $R - X$ is facilitated. Thus, rate decreases. This evidence of course confirms that S_N1 is a two step process.

2. Stereochemistry involved

Stereochemical observations give better picture to understand whether a reaction is S_N1 or S_N2.

S_N2: If the reaction starts with an optically active substrate, it will end with an optically active product. But the product has an inverted configuration. This is only possible when there is a backside attack and a transition state, not the intermediate is involved in the reaction.

S_N1: Racemisation is a definite outcome of S_N1 reaction. If the reaction starts with an optically active substrate, it will end with a racemic mixture (though 100% racemisation is not possible but of course, observed optical activity, if it is, will be very very less and hardly detectable. Even if it is detectable, the optical rotation is found to be reversed as the enantiomeric excess is due to the inverted configuration). In S_N1 reaction, as there is a carbocation intermediate, which is planar, there is a chance for front as well as back side attack which will result into the racemisation. As a planar carbocation intermediate is involved, hence S_N1 is a two step process.

3. Isotopic detection (α and β secondary kinetic isotope effects)

If at the β position with respect to the bond breaking position, a hydrogen atom is substituted with deuterium and the reaction is slowed down then definitely a carbocation is involved and hence it confirms that the reaction is multi-step in nature. This observation is very much found in S_N1 reaction but not in S_N2 reaction. In S_N1, k_H/k_D is very high for β secondary isotope effect.

On the other hand, if a hydrogen atom is substituted with deuterium at that carbon atom which is directly attached with the leaving group then any change in the reaction rate is termed as α isotope or
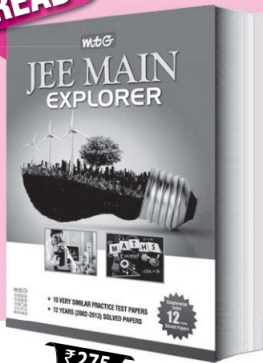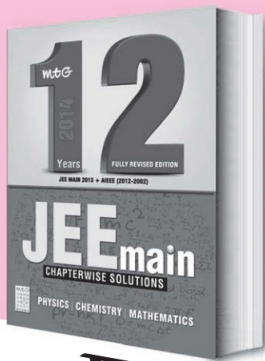
α isotopic effect. This is also found in S_N1 reaction and here k_H/k_D is quite high. But in S_N2, $k_H/k_D \approx 1$. So, again isotopic effects confirm that S_N2 is a single step whereas S_N1 is a two step process.

4. **Nucleophilic substitution promoters and salt effect**

There are certain salts on addition of which rate of S_N2 and S_N1 reactions can be promoted. They are called the nucleophilic substitution promoters and this is the salt effect.
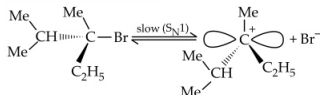
If this Br^- can be pulled away then it is easily understandable that the reaction will shift more to the forward direction. So, Ag^+ can be added to serve the purpose as Ag^+ is a good match for Br^- (according to HSAB principle). So, this will enhance or promote the rate of the S_N1 reaction. Such ions are the promoters. More examples are: Hg^{2+}, Hg_2^{2+}, Pb^{2+} (to some extent). Even H^+ acts as promoter specially when it is a question about pulling F^- (small in size, Ag^+ will not suit for this). So, after adding these ions, if the rate of the reaction is enhanced, then it is an S_N1 reaction for sure.

Now, what about S_N2 reaction? The presence of a very strong nucleophile gives a good platform for another nucleophile to attack the substrate. Such an example is azide ion (N_3^-) or alkyl sulphide (RS^-) ion.

Factors influencing relative reactivity of S_N2 and S_N1 reactions

(a) **Constitutional influence:** In bimolecular nucleophilic substitution reaction (S_N2), there is a simultaneous electron transfer from the nucleophile (substituting agent) to the alkyl group and from the alkyl group to the leaving group. These transfers are not in proper balance. On the other hand, in case of S_N1 reaction, in the rate determining step, there is only transfer of electrons from the alkyl group to the leaving group but there is no gain of electrons by the alkyl group. This is why in case of S_N1 reaction, a large kinetic polar effect is observed [i.e. ionization promotes the reaction], however, this is very less in S_N2 reaction. This is why structure of the substrate has to play a great role in determining the relative rate of reactivity of different substances in S_N1 and S_N2 reactions.

So, ultimately structure of the substrate has two major effects:

(i) *Electrical effect* (kinetic polar effect) : More profound in case of S_N1 reaction.

(ii) *Steric effect* : More profound in case of S_N2 reaction.

In case of S_N2 reaction, less steric hindrance is preferred. So, the preferred order is

methyl halide > 1° halide > 2° halide >> 3° halide

Aryl halides have almost the similar reactivity as 3° halides but it is dependent on the fact that what kind of substituted aryl group is present as well as along with the aryl group which other associate groups are present.

Here carbon is attached with four members — TS Here carbon atom is attached with five members
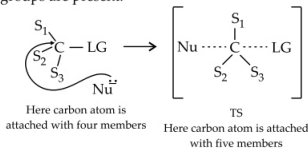
$\{S_1 \rightarrow$ substituent 1, $S_2 \rightarrow$ substituent 2, $S_3 \rightarrow$ substituent 3$\}$

In the substrate the carbon atom is surrounded by four groups whereas in the transition state it is surrounded by five groups. So, in the transition state steric crowding increases and as a result, energy of the transition state increases which in turn decreases the rate of reaction. Therefore, it is always good to start with less crowded substrate.

However, influence of steric effect is very less in case of S_N1 reaction as nucleophile is not involved in the transition state. Alkyl halides which have large substituents attached with it, experience back strain (B-strain). To get rid off it, release of halide group is accelerated so that the groups can place them at an angle of 120° in the planar configuration rather than placing them at 109.5° with each other in the tetrahedral configuration. This is known as steric acceleration. So overall, the order of reactivity of different alkyl halides is

In S_N2, 1° halide > 2° halide > 3° halide

In S_N1, 3° halide > 2° halide > 1° halide

(b) **Power or nature of the nucleophile:** Whether a nucleophile can control the rate of a reaction or not? For S_N1 of course it is not, as the nucleophile is not involved in the transition state. However, if there is a situation that to a particular substrate more than one nucleophiles are added then the

most powerful nucleophile will win the game and this will be the product.

In S_N2 reactions, nucleophiles have direct influence. The obvious reason for this is nucleophiles are involved in the rate determining step of S_N2 reaction.
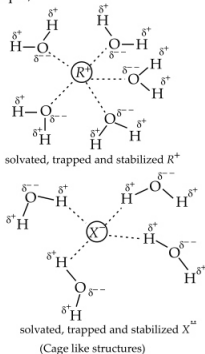
(c) **Nature of solvent:** Solvent plays a major role in nucleophilic substitution reaction as solvent is the reaction partner for nucleophiles.

In S_N1 reactions, ionization is a fundamental requirement. This can only be possible if the solvent is polar and holds a high value of dielectric constant. In the transition state of S_N1, a dipolar form of the substrate exists as in the following form:

Who gives guarantee that these will not go back to $R-X$?
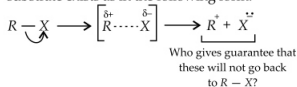
Guarantee is given by a polar solvent only as in that case the transition state as well as R^+ (also $\ddot{X}^-$) can be stabilized through dipole-dipole interaction.

For example,

solvated, trapped and stabilized R^+

solvated, trapped and stabilized $\ddot{X}^-$
(Cage like structures)

So, a polar solvent functions in two ways:

(i) Due to its high dielectric constant, it reduces electrostatic attraction force between the cation and the anion of the substrate.

(ii) Secondly, it stabilizes the cation and the anion. This is very important point as stabilizing cation and anion means to stabilize the transition state also as the transition state holds polar character.

So, which kind of solvent is required for S_N1

reaction? Polar protic or polar aprotic? Of course it is polar protic as polar aprotic solvent will fail to fulfill the second condition. Therefore,

Suitable solvents for $S_N1 \Rightarrow$ polar protic like
$$CH_3OH, C_2H_5OH, H_2O \text{ etc.}$$

Not suitable solvents for $S_N1 \Rightarrow$ non-polar and
polar aprotic like DMF, DMSO, CH_3NO_2 etc.

For S_N2, however, the idea is slightly different. Here, the substrate initially does not contain that much high polarity. High polarity of the substrate is also not a demand for S_N2 reaction. What happens is that the nucleophile attacks the partially positive carbon atom of the substrate which just starts to release the anion (leaving group). Due to the negative charge on the nucleophile whatever partially positive charge developed on the carbon atom that gets neutralized. So whatever polarity was there in the substrate, in the transition state it is lost. The transition state is carrying negative charge only. So, polarity of solvent cannot stabilize the transition state. This is why with the increase in the solvent polarity, reaction rate is found to decrease slightly as more polarity can stabilize the substrate better than that of the nucleophile.

can't be stabilized effectively with the solvent polarity
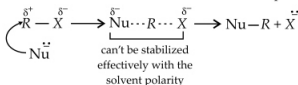
After so many of these facts there is still something to say about the protic and aprotic solvents.

How??

Like this,

$$\left(\text{DMF is } H-\underset{\underset{O}{\parallel}}{C}-\ddot{N}\underset{Me}{\overset{Me}{<}} \right)$$
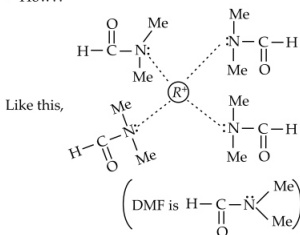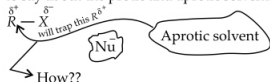
But, $\ddot{N}u$ will not be trapped and its attack becomes facilitated. Moreover trapping of R^+ helps to release $\ddot{X}^-$ faster which in turn increases the rate

of the reaction.

relatively naked
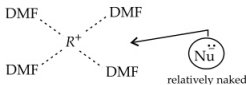
On the other hand, a protic solvent solvates both the cation and the anion and it traps the nucleophile. Hence, attack of the nucleophile gets retarded. Overall, the rate of the reaction is reduced.

Thus, for S_N2, solvents should be polar aprotic like DMF, DMSO, DMPU, DMA

where, DMPU = dimethyl propylene urea,

DMA = dimethyl acetamide.

Non-polar solvents should not be used, why?

Though solvent polarity slightly decreases the rate of S_N2 reaction but it is also found that polar (aprotic) solvent helps to stabilize R^+ which has great influence in the rate of the reaction. This is why polar (aprotic) solvents should be used instead of non-polar solvents.

Solvents that should not be used for $S_N2 \Rightarrow$ polar protic solvents

(d) **Nature of leaving group:** Fast the leaving group will leave, it will be easy for the nucleophile to take that place. For example, I^- is a better leaving group than F^- and here the order is $I^- > Br^- > Cl^- > F^-$. This is true for both S_N1 and S_N2.

Use the following data:

$$\text{Bond energy:} \quad \underset{55 \text{ kcal/mol}}{>C-I} < \underset{70 \text{ kcal/mol}}{>C-Br} < \underset{80 \text{ kcal/mol}}{>C-Cl} < \underset{110 \text{ kcal/mol}}{>C-F}$$

Both in S_N1 and S_N2, expulsion of leaving group (LG) is involved in the rate determining step. Apart from tosylate, brosylate, nosylate, mesylate and triflate, other two very good leaving groups are:

Nonaflate ion or Nonafluorobutane sulfonate ion

$$\left(\overset{..}{\underset{..}{O}} - \overset{\overset{O}{\|}}{\underset{\|}{S}} - (CF_2)_3CF_3 \right)$$
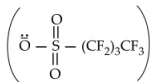
Tresylate ion or 2,2,2-Trifluoroethane sulfonate ion

$$\left(\overset{..}{\underset{..}{O}} - \overset{\overset{O}{\|}}{\underset{\|}{S}} - CH_2CF_3 \right)$$
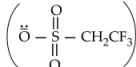
In general, the leaving group capacity (opposite to basicity) is

$NH_2^- < CH_3O^- < OH^- < PhO^- < NH_3 < CN^- < F^- < Cl^- < Br^- < I^-$.